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NITROGENOUS COMPOUNDS IN THE ENVIRONMENT

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NITROGENOUS COMPOUNDS IN THE ENVIRONMENT

by the

Hazardous Materials Advisory Committee

U.S. ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON D.C. 20460

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STUDY: NITROGENOUS COMPOUNDS IN THE ENVIRONMENT

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PREFACE

The Hazardous Materials Advisory Committee provides independent and expert advice to the Administrator of the Environmental Protection Agency on scientific and policy matters pertaining to hazardous materials in the environment. Early in 1972, the Committee began a study concerning the sources and effects of nitrogenous compounds in the environment.

The principal objective of the study is to inform the Administration about the nature of the problem and the perceived needs in terms of monitoring, research, and regulation.

Each section of the report was prepared by specialists in the various areas. Following a review of the report by members of the Hazardous Materials Advisory Committee in early 1973, Dr. Norton Nelson prepared the committee statement. It represents the best judgment of the committee relating to the possible development of policy regarding this matter.

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COMMITTEE STATEMENT

THE MANY FORMS OF NITROGEN are an integral part of our natural environment. A number of nitrogenous compounds are essential parts of all living systems. Partly for this reason, there has been since life began, an enormous natural nitrogen cycle in which nitrogen moves through the soil, water, atmosphere, and a myriad of life forms. These cycles are complex and involve enormous quantities of nitrogen, totalling millions of tons each year.

In part, it is this integral relationship to life that has produced local disturbances caused by excessive loads at certain locations within the nitrogen cycle in many places around the world. Non-biological factors--erosion, weather, and lightning--also contribute to the nitrogen cycle. The need to use fertilizers to improve agricultural productivity, in order to feed the larger populations that cluster more and more near urban centers, plays its part in altering the movement of nitrogen through the environment. Other sources of disturbances due to excessive enrichment have arisen through energy production. Combustion processes generally lead to the formation of nitrogen oxides produced from atmospheric nitrogen. Accordingly, the internal combustion engine, heating, and power production from fossil fuels are all significant contributors to alterations in the nitrogen cycle.

The growth in population; the concentration in and around urban centers; and the need to produce food, to keep warm or cool, to produce electricity, and to move about in our automobiles are all capable of adding to the nitrogen load that must be assimilated by the environment. Most of the manifestations tend to be localized. The significance of these disturbances has begun to be recognized only recently.

At present, all known trends appear to be ones that can be managed and kept within control, if appropriate steps are taken now. In the following sections of this statement, some of these major responses that are needed will be identified. Each of the papers in this report should be examined for details on the present status and on the responses needed, in relation to man's effect on the movement of nitrogen through the environment.

MUNICIPAL DISCHARGES INTO WATER AND SOLID WASTE

Human wastes constitute a major contribution to the nitrogen burden in water. For example, the nitrogenous material discharged from sewage-treatment plants in the United States amounts to 0.45 million metric tons per year. This quantity could raise the nitrogen content of that third of the total annual precipitation in the United States which is used by man up to the limit set by the Public Health Service for nitrogen in drinking water--10 milligrams per liter.

The problem at present in many areas is the concentration of several discharges into restricted parts of waterways. The technology for the denitrification of such discharges is still primitive and inadequate. The recovery of nitrogen for useful purposes (say, in agriculture) is still not generally economical from the producer's standpoint.

In monitoring the efficiency of waste-water treatment plants, the critical problem is the fact that the commonly employed biochemical oxygen demand (BOD) test does not measure nitrogen reduction.

The undesirable consequences of municipal discharges are: (1) in some areas, the nitrogen concentration in drinking water is raised to an unacceptable level; and (2) such discharges can contribute to increased nutrient levels in natural waters to such a degree that this leads to undesirable biological changes, such as algal blooms.

To improve municipal sewage-treatment systems:

1. Greater consideration should be given to the effectiveness of the denitrification process in the design and operation of sewage-treatment plants.
2. Tests for nitrogen species should be conducted in order to monitor the effectiveness of nitrogen reduction in sewage-treatment plants.
3. The nitrification effects in the biochemical oxygen demand (BOD) test should be eliminated.
4. Improved procedures for denitrification need to be developed.
5. Effective and economical means for collecting and converting nitrogenous wastes in wastewaters and sludge into useful purposes are also needed.

A secondary municipal source of nitrogenous material reaching ground and other waters is that which is leached from sanitary landfills. The resolution of this problem will require:

1. More thoughtful planning in determining where landfills can be located safely, without leading to undesirable nitrogen discharges into local waters.
2. The development of techniques for inserting covers that are water-impermeable but are gas-permeable, in order to prevent the contamination of local water.

NITROGEN DISCHARGES INTO THE ATMOSPHERE

The presence in and movement through the atmosphere of nitrogen compounds is part of the natural nitrogen cycle. As noted previously, however, man has altered this cycle, at least locally, in a number of ways. Of prime importance is the oxidation of atmospheric nitrogen during combustion processes into the nitrogen oxides, primarily nitric oxide (NO) and nitrogen dioxide (NO_2). Enormous quantities of these oxides are formed by combustion in space heating, power production, and the operation of internal combustion engines.

Nitrogen dioxide is directly toxic to man. At relatively low concentrations, it can contribute to respiratory disease. In addition, it is directly involved in the formation of photochemical smog through a series of complex atmospheric and photochemical reactions. These can produce nitrous and nitric acids, too; also, peroxyacetyl nitrate (PAN)--which, like NO_2, produces plant damage, but at much lower concentrations. As air pollutants, the nitrogen oxides have received prominent attention in federal air-pollution legislation. Major steps aimed at control are now under way. The technology for such control, however, appears to be inadequate in terms of efficiency as well as cost. Also, the data correlating ambient levels of nitrogen oxides, particularly nitrogen dioxide, with adverse health effects are inconclusive.

These requirements are evident:

1. The human health effects of nitrogen oxides and PAN need further study, particularly for long-term exposures to ambient levels of these pollutants.
2. The synergisms for humans and for plants between these compounds and other air pollutants also need further study.
3. The chemical and physical transformations of these compounds, as well as nitrous and nitric acid, need further study under real and simulated atmospheric conditions.
4. More effective and economical control procedures for limiting the discharge of nitrogen oxides must be sought for combustion processes (power production, space heating, the internal

combustion engine, and so on).

5. Measures must be taken to insure that the use of control devices (catalytic converters on automobiles) do not add additional pollutants (NH_3 and N_2O) to the atmosphere.

DISCHARGES OF NITROGEN INTO THE ENVIRONMENT FROM CROP PRODUCTION

The use of nitrogen-containing fertilizers has been a major source of the substantial increase in agricultural productivity over the last century in the United States. Our nation's food supply would be greatly affected by a drastic curtailment in the use of nitrogen fertilizer.

On the other hand, our high preference for proteins of animal origin have led to a considerably greater nitrogen requirement than would be the case if our national diet were based primarily on plant proteins. This dietary preference and the population growth have increased the need for available nitrogen on the farm by almost 8 million tons since 1940 (NAS-NRC Report on Accumulation of Nitrate, p. 37). That is almost a doubling of the requirement for the use of such nitrogen during the period.

Although many studies have been conducted in recent years on the effect of fertilizer use (or misuse) on nitrogen levels in waterways, the effect is still not well defined. It is apparent that in some regions (depending on agricultural practices, soil types, rainfall, and drainage patterns), there can be significant, undesirable nitrogen levels in both surface and ground water.

It would be useful, therefore, to:

1. Better define the regional patterns of nitrogen concentration in water--especially in ground water, which has received little attention.

2. Determine the significant factors contributing to such concentrations.

3. Study more thoroughly the relative crop-yield efficiency as well as the nitrogen-contamination potential of different nitrogen fertilizer compounds, rates, times, and methods of application.

4. Continue research on the maximum loading of animal and human wastes on crop land.

5. Determine the patterns of nitrogen use that take into account the efficiency aspects of food production, the maintenance of soil productivity for future generations, and the environmental effects.

6. Develop efficient means of helping producers to reliably determine the actual nitrogen requirements in a particular set of circumstances (crop, region, field, and the like) and make this information conveniently available, so producers can carefully adjust applications of nitrogen (with chemical fertilizers, and by using animal and human wastes) to actual needs.

For a variety of reasons, these objectives cannot be determined or accomplished all at once. However, a major program is needed.

DISCHARGES INTO THE ENVIRONMENT FROM ANIMAL WASTES

The contribution of nitrogen from animal wastes is substantially greater than that from human wastes. An estimated 6 million metric tons of nitrogen are produced annually from this source in the United States. Although the N in livestock waste amounts to many times more than that arising from human wastes, it is usually distributed over the land, while human wastes are often discharged into surface waters with little or no treatment to remove the nitrogen.

Our preference for meat and other animal proteins is responsible for the very high livestock production in this country, which is proportionately much greater than that in most of the rest of the world. The problem has been intensified in recent decades with the growth of livestock production and with the increasing pattern of concentrating such production in large confinement operations. This had led to locally high concentrations of nitrogenous compounds in the water and in the atmosphere.

Additional effort to appropriately manage the problem of animal wastes will require the:

1. Development of economically acceptable means of recycling livestock wastes for use in crop production or for conversion into usable protein by bacterial protein production or by other, still-undefined means.
2. Development of practical means for converting livestock waste into fuel through anaerobic decomposition or pyrolysis (burning).
3. Development of denitrification procedures that are economical as well as feasible.

INDUSTRIAL DISCHARGES

These discharges of nitrogen compounds can be considered from several aspects. Such discharges add to the available nitrogen in aquatic systems, increasing the load being generated from other sources such as human and animal wastes and fertilizer. The magnitude and the extent of the nitrogen-discharge contribution to the nutrient source varies dramatically from one industry to another.

The array of synthetic chemicals, their byproducts, and the altered forms of these chemicals, which by direct loss in manufacture or disposal, also lead to chemical discharge into the environment from industrial processes. The problems presented by these compounds depend entirely on their specific chemical properties and on their toxicity to various life forms.

Thus, these nitrogen-containing compounds are simply a subclassification of all industrial chemicals. Accordingly, they require the same scrutiny and control as do other industrial chemicals that generally enter the environment. The fact that the synthetic compounds contain nitrogen does not merit placing them in any special category.

The proposed legislation on the control of toxic substances would provide a way of dealing directly with these issues. Industrial chemicals which contain nitrogen--other than those which alter the nutrient levels as noted previously--need no special consideration here.

DETRIMENTAL EFFECTS OF NITROGEN COMPOUNDS IN AQUATIC SYSTEMS

Compared to man, aquatic organisms are in some ways less tolerant of alterations in nitrogen concentrations. Although man seems to be able to readily tolerate 10 mg/l of nitrogen in drinking water (the 1962 Public Health Service Standard), such concentrations can severely affect the balance of life forms in aquatic systems. Two particularly undesirable results lead to major shifts in aquatic life and the production of algal blooms.

Avoiding severe disturbances in aquatic life may be the major, limiting factor in nitrogen control in aquatic systems. This sensitivity results primarily from an alteration in the nutrient sources available to aquatic life forms. In addition to this disturbance in nutrient levels, some forms of nitrogen are toxic to aquatic life. For example, ammonia can be toxic at quite low concentrations. On the other hand, little is known about the toxicity of the nitrite ion. Certain industrial nitrogenous chemicals discharged into aquatic systems can also be toxic.

Nitrogen concentrations that are detrimental to many forms of aquatic life are now occurring in waterways. This may bring about shifts in the abundance of species that cause nuisance growths. Some of these, such as certain species of blue-green algae, produce substances that are toxic to many forms of aquatic life as well as to terrestrial organisms. If detrimental effects to aquatic life are to be avoided, a number of requirements should be considered, depending on the particular situation. In some instances, the requirements listed here may be too strict because one cannot universally establish a concentration of N that will prevent algal blooms in all kinds of water. Accordingly, there is a need to pursue further the study of the toxicity of selected nitrogen compounds discharged into or present in aquatic environments.

The following requirements should be given consideration in making decisions regarding the avoidance of detrimental effects of nitrogenous compounds to aquatic life.

1. Maintain N as NO_3 and/or NH_4 at the beginning of the growing season to less than 0.3 mg/l in lakes and not more than 1 mg/l in free-flowing waters, or to carry out Provisional Algal Assay Procedure (PAAP) tests to determine what level of nitrogen is likely to cause eutrophication.
2. Maintain levels of un-ionized ammonia to less than 0.02 mg/l, unless it can be shown that it is not toxic to aquatic life.
3. Maintain the approximate N:P ratios characteristic of natural waters in the area.

ANIMAL HEALTH

High levels of nitrate and forage have led to toxicity and livestock loss. The difficulty arises from the bacterial conversion of nitrate in the forage into nitrite in the herbivore. The nitrite so formed leads to methemoglobinemia, which in severe cases can be fatal. Such episodes have been sporadic and localized. Both natural soil nitrate and nitrate derived from animal and human wastes and from fertilizers can contribute to high nitrate levels in the plants on which the animals graze. The nitrate level in the plant tends to increase during times of drouth, leading to a higher risk of poisoning during such periods.

Nitrosamines can be formed from the simultaneous ingestion of nitrite and secondary amines, possibly resulting in the formation of carcinogenic compounds. The role of these compounds in the induction of cancer in livestock is unknown.

1. Efforts to inform livestock producers about the risk of high nitrate levels in feed should be continued and extended.
2. Research should be undertaken to identify the significance of nitrosamines as possible causes of cancer in livestock.

NITROGEN COMPOUNDS AND HUMAN HEALTH

There are a number of ways in which nitrogenous compounds may affect human health. The first and best understood way relates to a poisoning known as methemoglobinemia, which is particularly likely to occur in infants. Another is the possible role of carcinogenic nitrosamines in the induction of human cancer.

Infants can be uniquely efficient in the conversion of ingested nitrate to nitrite, which in turn reacts with hemoglobin to form methemoglobin--thus reducing the oxygen-carrying capacity of the blood. Infant poisoning has been observed primarily from contaminated water supplies, and in a few instances from vegetables containing high concentrations of nitrate. These have been acute episodes. Little is known about the possible importance of chronic toxicity from lower levels of methemoglobinemia.

Within the last decade, a group of chemicals known as nitrosamines have been shown to be potent carcinogens in animals. The ingestion of nitrite with certain secondary amines can lead to the formation of these carcinogenic nitrosamines in animals. In some foods, they are found preformed in low concentrations. Consequently, concern has increased about the widespread use of nitrite and nitrate in foods, especially in cured meats (wieners, ham, bacon, and the like). This usage is primarily to inhibit the growth of *C. botulinum* microorganisms. Furthermore, nitrites impart a red color and cured flavor.

1. The present drinking-water standard of 10 mg/l of nitrate nitrogen should not be relaxed, but research should be continued to establish more precisely the levels that are likely to result in methemoglobinemia in infants.
2. Educational efforts by pediatricians and public health nurses about the danger of preparing infant formulas from contaminated water should be continued and extended.
3. Analytical techniques to determine the presence of nitrosamines need to be improved and their application extended, including the presence and extent of nitrosamines in foodstuffs.
4. Studies on the likelihood of nitrosamine formation in humans from ingested chemicals need to be continued and accelerated.
5. The role, if any, of the contribution of nitrosamines to human cancer also needs study.

ANALYTICAL PROCEDURES

Despite the long history of concern with nitrogenous compounds in agriculture, in air and water pollution, in waste treatment, chronic toxicity from lower levels of methemoglobinemia.

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5. The role, if any, of the contribution of nitrosamines to human cancer also needs study.

ANALYTICAL PROCEDURES

Despite the long history of concern with nitrogenous compounds in agriculture, in air and water pollution, in waste treatment, and in relation to human health and environmental effects, many inadequacies and inefficiencies remain in the availability of analytical techniques to monitor and assess the various facets of nitrogen and its movement through the environment. These are discussed herein, and some proposals for the correction of these defects are made.

ABSTRACT

THIS REPORT is a series of papers on the sources and methods of control and the environmental and health effects of nitrogenous compounds. Diverse aspects of municipal and industrial sources are discussed--waterborne, atmospheric, agricultural, and industrial processes generating nitrogenous compounds. Attention is given to nitrogenous materials in waste and surface waters, efficiency of sewage treatment, effectiveness of the conventional BOD test, and the contribution of urban runoff and landfill leakage to the overall nitrogen load in the environment. Concentrations, sources, sinks, the transformation of nitrogenous materials in the lower atmosphere, control measures for stationary and mobile sources, retrofit systems for used cars, and new engine systems are reviewed. Plant nutrients, including fertilizers, and animal wastes are considered. The growing problems resulting from concentrated centralized livestock feedlots and methods of control are pointed out.

Nitrogen is discussed as a nutrient essential to living organisms and as a toxicant within the aquatic environment. The carcinogenicity of nitrosamines and their precursors is described as a potential danger to health.

Individual nitrogenous compounds are appropriately identified throughout the report. Analytical procedures for the identification and quantification of nitrogenous compounds are reviewed.

As presented to the Environmental Protection Agency in this report, the statement of the Hazardous Materials Advisory Committee presents the major concerns regarding nitrogenous compounds in the environment as these relate to the following Agency activities: research, monitoring, and regulation.

Municipal and Solid Wastes

Sources of Nitrogenous Compounds and Methods of Control

HAROLD WOLF

WATER-BORNE NITROGENOUS MATERIALS FROM MUNICIPAL AREAS

THERE ARE TWO BROAD GROUPS of such nitrogenous materials: those present in wastewater and those in surface runoff. The concentration of nitrogenous materials found in wastewater varies considerably less than that in runoff[1]. Man's knowledge about the relationship of the simpler forms of nitrogen to the biological-oxidation processes of sewage treatment has a longer record than his knowledge of the biochemical oxygen demand (BOD) associations. Prior to the use of BOD procedures, the oxidation of the ammonia (NH_3) in sewage into nitrate (NO_3) formed the basis for the design and operation of wastewater treatment plants. Nitrogenous materials in runoff, on the other hand, have been studied only recently.

This part of this paper deals mainly with the wastewater aspects of nitrogenous compounds, aerobic as well as anaerobic. Two types are considered: the point-source discharges into surface water from sewage treatment plants, and the smaller and more disperse discharges made through anaerobic processes into ground water. The nitrogenous portions of urban runoff and sanitary-landfill leachate and analytical problems are also reviewed.

NITROGENOUS MATERIALS IN SEWAGE

Nitrogen can exist in seven states of valence:

NH_3	N_2	N_2O	NO	N_2O_3	NO_2	N_2O_5
3-	0	1+	2+	3+	4+	5+

Compounds of nitrogen in the 1+, 2+, and 4+ forms appear to have little significance in the biological processes generally used in sewage treatment, aerobic or anaerobic[2]. The analytical procedures commonly used in practice determine NH_3-N, organic N, NO_2-N, and NO_3-N (see the section of this paper on analytical problems). Total Kjeldahl nitrogen (TKN) is often used to

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express NH_3-N plus organic N. Dissolved N_2 is practically always ignored, although it has received some attention recently because of fish kills caused by the supersaturation with N_2 of river waters downstream from dams[3].

Approximately 80 percent of the total nitrogen in domestic wastewater originates as urea. An adult male excretes about 1,500 milliliters of urine a day. The nitrogen-containing components expressed in grams include urea, 30; uric acid, 0.7; creatinine, 1; ammonia, 0.7[4]; and undetermined N, 0.9[5,6].

	Percentage of nitrogen
Urea	47
Uric acid	33
Creatinine	37

Nitrogen is also contributed from feces. The daily, per capita excretion of feces on a dry-weight basis is 25 to 50 grams. Of this, total nitrogen averages 1.3 grams per day[5]. Correcting for the various molecular weights, the total nitrogen output for an adult male--both urine and feces--is on the order of 16 grams per day. This value is supported by figures given in a recent National Academy of Sciences' publication[7]. The estimate shown was that 1.1 million metric tons of nitrogen are produced each year by 202 million Americans, or about 15 grams per day per person.

If we assume that the average amount of water used per capita in a municipal area is 100 gallons per day[8], 15 grams of nitrogen would produce a concentration of 40 milligrams per liter. By comparison, a 1937 committee report of the American Society of Civil Engineers cites 35 mg/1[9]; Weibel cites 40 mg/1[10]; and Keup and MacKenthun cite 34 milligrans per liter[11].

Weibel's review indicates that in raw wastewater, inorganic N (the sum of nitrite, nitrate, and ammonia as N) constitutes about three-fourths of the total nitrogen[10]. Others suggest that total N is about equally divided between ammonia and organic N, with negligible nitrite and nitrate levels[9,12].

Hanson and Lee[5] studied the nitrogen content of the wastewater from two Wisconsin communities. Total N as used in their paper is equivalent to TKN. The organic N procedure also includes urea. Their findings:

Percentage distribution by type of nitrogen

	NH_3-N	Urea-N	Total amino acid-N	Sum
Madison	60	7.6	12.5	80.1
Cross Plains .	60	14.5	7.1	81.6

Thus, approximately 20 percent of the total N in each wastewater was not identifiable. (Hanson and Lee did not consider inorganic N or nitrates, nitrites, or dissolved N_2 as part of total nitrogen.) They speculated that some of the unaccounted-for N might be heterocyclic nitrogen compounds or complexes--formed by reaction with phenolic substances, lignins, tannins, or quinones. Quite obviously, they conclude, other chemical forms of nitrogen that are measured by the organic-N procedure remain to be determined.

Total (dissolved plus suspended) alpha amino acid-N ranged from 14 to 44 percent of organic N for Madison, and 15 to 26 percent for Cross Plains. A few analyses for hexosamine-N revealed insignificant quantities. Alpha-amino acid-N probably includes mucopeptides and teichoic acids, important constituents of bacterial cell walls. Mucopeptides, in turn, include amino acid complexes containing an amino sugar and muramic acid--the latter having been detected in wastewater. Some nitrogen may exist as chitin, a polymer of N-acetyl glucosamine. Other N-containing compounds present in sewage are the nucleic acids--adenine, guanine, cytosine, thymine, and uracil, as well as xanthine, hypoxanthine, histamine, indole, and skatole.

Urea is readily hydrolyzed into ammonia by the enzyme urease. The relative quantities of urea and ammonia in the sewage arriving at a sewage treatment unit may be a function of the travel time. This was offered as an explanation of the lower urea finding for sewage from Madison versus Cross Plains by Hanson and Lee. However, the lowered urea was not reflected in higher ammonia concentrations; rather, in a higher amino-acid nitrogen.

The chemical qualities of domestic wastewater can be influenced markedly by the industrial wastes that are discharged into municipal systems. The Madison plant receives wastes from a meat packer (11 percent of the total flow), a metal-working plant, and a battery producer. For the last two the organic contribution is understandably reported as quite low. The Cross Plains plant receives wastes from a creamery (18 percent of the total flow). The meat packing plant and the creamery would both add substantial organic loads to the sewage plants, but the packing plant might be expected to exert greater influence on the alpha amino-acid N concentrations, which is borne out by the analyses.

The influences of industrial wastes on the nitrogenous characteristics of municipal wastewater are such that they are better considered plant-by-plant. Therefore, these influences are excluded from this part of the paper.

MUNICIPAL SEWAGE TREATMENT PROCESSES

Primary treatment. Once wastewater is in the sewage treatment plant, it is generally exposed first to the anoxic conditions of grit chambers and primary settlers. These processes have practically no effect on the ammonia concentration at the near-neutral pH levels that generally exist. If the pH value were higher, a slight reduction might be observed because of the equilibrium reaction:

$$\underset{\text{lower pH}}{NH_4^+} \rightleftharpoons \underset{\text{higher pH}}{NH_3 + H^+} \qquad (1)$$

Since ammonia is highly soluble and the surface:volume ratio of primary tanks is very low, little ammonia will be released. For example, at two plants in Dallas, Texas, the ammonia gain or loss in primary treatment is quite closely related to the pH range observed:

	Year	NH_3 gain (+) or loss (-) mg/l	pH range
White Rock	1970	-0.2	7.1 to 8.1
White Rock	1969	-0.1	7.1 to 8.0
Dallas	1970	+0.1	6.5 to 7.6
Dallas	1969	0.0	6.8 to 7.8

Since both plants employ recirculation and also send secondary solids to the digestors through the primary units, these data would not be applicable to other primary processes. Although primary sewage treatment has little effect on ammonia concentrations, it does result in a substantially lowered organic-N concentration, because of materials that settle-out or float and which are subsequently removed mechanically to sludge-handling facilities. For the same Dallas plants, these percentage of organic-N reductions were observed:

	Year	Pct. reduction, organic N
White Rock . . .	1970	34
White Rock . . .	1969	29
Dallas	1970	28
Dallas	1969	27

Since practically no change in concentrations of reduced (ammonia) or oxidized (nitrite or nitrate) nitrogen forms occurs in primary processes, little biochemical activity involving N-forms takes place during this phase of sewage treatment.

Secondary treatment. The next step in the treatment of wastewater is generally an aerobic biological process. Considerable changes in N forms occur, with the amount of change varying markedly according to the individual plant and its operation.

In either aerobic or anaerobic environments, organic N is converted into ammonia[2]:

$$\text{Protein (organic N)} + \xrightarrow{\text{bacteria}} NH_3 \qquad (2)$$

Under aerobic conditions, nitrite formers can carry out the next reaction:

$$NH_3 + 3O_2 \xrightarrow{\text{bacteria}} NO_2^- + H^+ + H_2O \qquad (3)$$

A second group of nitrifying bacteria then can complete the nitrification process:

$$2NO_2^- + O_2 \xrightarrow{\text{bacteria}} 2NO_3^- \qquad (4)$$

Biological Processes 2, 3, and 4 are carried out to various degrees in sewage treatment plants. The effectiveness of sewage treatment is conventionally measured by the BOD test, which may or may not reflect the nitrogenous oxygen demand of the sample. If nitrifying organisms are absent or if too few of them happen to be in the sample bottle, the result will not express the nitrogenous oxygen demand--which can be considerable. A more complete discussion of the relationships involved may be found in a recent article by James C. Young[33].

The nitrification processes are slow in comparison to carbonaceous oxidation, and are quite susceptible to the effects of heavy metals[13]. The first manifestation of an influx of toxic metals into a nitrifying sewage treatment plant is the inhibition of nitrification.

These are some recent observations at the Dallas Water Reclamation Research Center about the effects of nitrification on various factors:

1. Highly nitrified ($NH_3N < 1.0$ mg/l), activated-sludge effluents display four times the metals removals (average of all metals observed) of less-nitrified ($NH_3N > 8.0$ mg/l) effluents.
2. Carbon adsorption also displays different performance in metals removals--the higher ammonia effluents resulting in poorer removals for some important metals, such as cadmium and lead.
3. Highly nitrified, activated-sludge plant operation decreases the refractory chemical oxygen demand (that COD which passes through carbon adsorption processes) by half or two-thirds, compared to non-nitrified operation.
4. The number of bacterial viruses present in the discharge from a highly nitrifying activated sludge plant is markedly less than that from a non-nitrifying plant.
5. The ammonia present in non-nitrified discharges combines with chlorine to form chloramines; and chloramines--although effective against the coliform-indicator organisms--are relatively useless in eliminating viruses.

Nitrification is also dependent on pH and temperature. In some sewage lagoons during the winter months, NH_3 concentrations will increase because the nitrifiers are slowed down. As the temperatures rise, the nitrite-forming bacteria become active and produce more nitrites. The remaining nitrifiers will become active and complete the reaction. If the warming occurs rapidly, it is possible for a rather high nitrite concentration to exist for a few days. In a nitrification process, however, nitrites are usually present only in concentrations of less than 1 milligram per liter.

Reactions occurring among the nitrogenous materials can be summarized as:

$$\begin{aligned}&\text{Organic N} \;\substack{\text{oxidation}\\ \text{reduction}}\; \text{NH}_4^+ + \text{organic N} \xrightarrow{\text{oxidation}} \text{NO}_2 + \\ &\text{organic N} \xrightarrow{\text{oxidation}} \text{NO}_3 + \text{organic N}\end{aligned} \qquad (5)$$

The residual organic N that carries through the biological treatment process is called "refactory." Data do not always reflect this terminology, however, because the more complete the oxidation process is, the smaller the amount of organic N that will be present in the discharge.

The "nitrogen effectiveness" of different types of sewage treatment processes can be illustrated by performances observed in Dallas, Texas. The Dallas plant is a standard-rate, trickling-filter plant--the most-common type seen throughout the United States.

Dallas Plant

	Pct. reduction		Effluent concentration
	NH_3-N	Organic-N	NO_3-N (mg/l)
1970	45	49	3.6
1969	44	45	3.2

The White Rock plant is a two-stage, high-rate plant that is organically overloaded.

White Rock Plant

	Pct. reduction		Effluent concentration
	NH_3-N	Organic-N	NO_3-N (mg/l)
1970	12	22	1.4
1969	11	25	0.9

These results can be compared with those obtained from an activated sludge process. A pilot unit in Dallas receiving primary effluent from the White Rock plant and operated so it produces a highly nitrified effluent (the slow growth rate of nitrifying bacteria requires longer reaction times) gave these results

Reduction in NH_3-N (pct.)	94
Reduction in organic-N (pct.)	63
NO_3-N in final effluent (mg/l) . . .	9.5

When a different bioreactor employing a much shorter reaction time was used, the following results were obtained, using the same influent:

Reduction in NH_3-N (pct.)	24
Reduction in organic-N (pct.)	25
NO_3-N in final effluent (mg/l) . . .	1.2

There is a considerable nitrogen significance involved in this shorter-reaction-time operation, a process termed "high-rate treatment." For a lower cost, the high-rate treatment will achieve a greater percentage removal of the biodegradable carbonaceous material than older processes, but at the expense of the nitrogenous material. The additional effectiveness is achieved through a better separation of the solids. The difference is the absence of "rising" sludge, which is associated with settling-basin denitrification[2,14]. The increasing application of the high-rate treatment is one of the reasons why the National Technical Advisory Committee on Public Water Supplies included the statement, "Greater attention to the design and operation of waste treatment plants for the oxidation of ammonia and organic nitrogen is needed to minimize the concentration of these pollution forms in receiving waters"[15]. The Iowa Water Pollution Control Board has recently adopted a regulation limiting ammonia in discharges[16].

This overall reaction is involved in sewage treatment:

$$\text{Org. N} \rightarrow NH_3 \rightarrow NO_2 \rightarrow NO_3 \qquad (6)$$

Environmental problems exist with respect to this reaction and all chemical forms of nitrogen. Biodegradable organic N will exert an oxygen demand on a receiving water. Organic N interferes with the chlorination process, which is reflected in part of the chlorine demand. The chlorine demand must be satisfied before efficient bactericidal activity can take place. Hence, organic N reflects a direct economic penalty. NH_3 is quite toxic to fish. It also interferes with the chlorination process by combining with the more effective disinfectant HOCl and forming a chloramine that has lesser disinfecting properties. Chloramine is also toxic to fish--but so are NH_3 and HOCl! The NH_3 discharged into streams will be oxidized by nitrifiers so that it, too, exerts an oxygen demand. Although NO_2 still has one more oxidative step to go, the effect of its oxygen demand is much less than that of NH_3.

The importance of NO_2 is recognized in the preliminary version of the new Drinking Water Standards to be issued by the Environmental Protection Agency. NO_2 is limited to 1 mg/l of the allowable 10 mg/l of NO_3-N where infants will be ingesting the water. Finally, the NO_3 form, which is highly stable and soluble, serves as a necessary plant and algal nutrient. In the anoxic environment of the intestinal tract, it can be reduced to NO_2--which is a mechanism of methemoglobinemia.

ADVANCED WASTE TREATMENT

Unit processes other than those just described can be applied to sewage-treatment-plant effluents in order to obtain further control. These are generally spoken of as "advanced waste treatment," or "tertiary systems." Such systems are not widely employed at this time; however, there is no question that they will be widely adopted in coming years. Increasingly, the direction of our program to control water pollution is being oriented toward the control of specific nutrients, mostly for phosphorus at present.

Tertiary treatments use processes that are nonspecific for nitrogenous materials, as well as ones developed specifically for nitrogen removal. The former include rapid sand filtration of activated-sludge effluents; chemical coagulation and precipitation using lime, polymers, or iron or aluminum salts, or various combinations thereof; activated-carbon adsorption; and nonspecific dimineralization. The nitrogen-removal processes include ammonia-stripping, ion-exchange, biological nitrification, and breakpoint chlorination. The results that can be expected from these processes often vary according to where they are used, their location in the treatment sequence, and the quality of the water involved.

An effective means of increasing our control of water pollution would be to filter activated-sludge plant effluents. The utility of this treatment has been under study in Dallas for several years. Filtering the effluent of a nitrifying activated-sludge plant through sand and anthrafilt gave the following data for September, 1972:

Nitrogen forms, mg/l

	NH_3-N	Organic N	NO_2 and NO_3 as N
Influent	1.5	3.8	15.7
Effluent	1.3	2.9	16.3
Pct. removal	13.3	23.7	+3.8

A substantial, additional increment of organic N was removed by filtration. The fact that nitrification was proceeding in the filter was demonstrated by the increased amount of NO_2 plus NO_3 in the effluent, an indication that the water applied to the filter still contained a substantial amount of dissolved oxygen and/or little degradable carbon.

It is possible to design and operate an activated-sludge filtration system for denitrification. The activated-sludge plant would be designed to nitrify; and the filters, to denitrify[17]. Such a system was first suggested by Parkhurst *et al.* as a result of their Pomona studies[18].

In Dallas, the filtration of trickling-filter effluents was demonstrated to be impractical. The filters quickly blind due to the nature of the suspended materials applied. However, this does not necessarily mean that it would be impractical to filter all trickling-filter effluents. More study is needed by others in order to evaluate this possibility. In Dallas, it is necessary to provide chemical pretreatment with coagulants--such as in water treatment processes--in order to achieve a filterable water. A number of short runs utilizing iron salts and lime made on the final effluent at White Rock showed an average organic N removal of about 30 percent. Chemical treatment together with filtration provides for 40-percent removal, down to an effluent concentration of 2 to 3 milligrams per liter.

Granular activated carbon can be used to achieve additional removal of organic nitrogen. In general, this type of treatment removes about half of the applied organic nitrogen. Granular carbon can be used as a filter. It will function both as a filter and as an adsorber; consequently, the removal of organic N would be somewhat higher. However, the carbon must be periodically regenerated when it loses its sorption capacity, and this regeneration process is a comparatively expensive one.

Nonspecific demineralization processes include distillation, electrodialysis, reverse osmosis, freezing, and ion-exchange. "Nonspecific" as used here means that these processes remove other impurities along with the nitrogenous materials. The processes just listed all represent another generation in costs, and are not likely to be applied generally to water discharged into the environment. Their proper place is in treating water for subsequent domestic or industrial use. In passing by these processes, it is of interest to note that ammonia N cannot be removed by the distillation process unless the feed water is first acidified (see Reaction 1) to maintain the nitrogen in ammonium form[19].

Ammonia-stripping has been used with varying degrees of success at the South Lake Tahoe plant[20]. The process is applied to a non-nitrifying, activated-sludge plant effluent. The pH of the water must first be elevated to about 11 (see Reaction 1). Cold weather sharply curtails the efficiency of the process, even in the absence of freezing. Efficiency is so low (30 percent) when the ambient temperatures are below freezing that little is gained. Yet, the process can achieve a 90-percent removal quite easily in warmer weather.

NOTE: The non-nitrifying operation of an activated-sludge plant allows about half of the organic N to pass undegraded. The stripping tower itself has no effect on the organic N[20], but the high pH treatment of the applied water may result in the hydrolysis of some of the nitrogen forms[21].

A selection ion-exchange process to remove ammonium has been developed by Battelle Northwest, and is being considered for full-scale use at Tahoe[20].

After various nitrogen-removal processes were reviewed by researchers at the Blue Plains plant for Washington, D. C., they determined that biological nitrification-denitrification was the most appropriate one for their needs. The nitrification aspect has been discussed under secondary treatment. The denitrification operation can be carried out in either suspended-bed or fixed-bed systems.

The former was selected for Blue Plains, where its operation is under intensive study. The investigators report periodic difficulty with erratic performance, but hope to achieve a consistent level of 2 mg/l or less of total nitrogen in the effluent. This would be a 91-percent removal of nitrogen, the most effective treatment reported[22], and represents an approach that will have to be initiated elsewhere.

Granular activated carbon, sand, gravel, and the like can all serve as fixed-bed denitrifiers under the proper conditions[17]. Such conditions include enough biodegradable carbon to support the denitrifiers (which generally means that some has to be added), a low amount of dissolved oxygen, and nitrogen in an oxidized form. Although a 90-percent removal of an applied 20 mg/l concentration has been reported with water[17], general data are limited concerning sewage[18].

Breakpoint chlorination can be used to eliminate the residual ammonia in an effluent. This treatment is under consideration at both Blue Plains and Tahoe, following their N-removal processes. A chlorine dose of more than 8:1 as a weight ratio of $Cl:NH_3$-N is required, and the treatment does not remove the organic nitrogen[23]. At Dallas, ozone will be studied for its effectiveness in removing nitrogen.

ANAEROBIC PROCESSES

Under aerobic or anaerobic conditions, as already stated, bacteria can convert organic N into ammonia. Septic tank processes are, of course, anaerobic processes. They are used for individual-household or for small sewage-treatment applications. Most often, the water coming out of septic systems is leached into the soil, which functions in an aerobic manner. When such applications are relatively isolated and carefully located with respect to individual ground-water supplies, little effect is observed. When such use becomes more concentrated, as has been the case in some suburban-type developments, the quality of the ground water can be reduced substantially. This has been observed for coliform concentrations and surfactants, as well as for nitrates.

Another widely used application of the anaerobic process is the sludge digestion employed at most sewage treatment plants. Sludge digestion is properly considered as a solids-handling problem. However, for the purposes of this paper, the contents of the digestion tank are considered in the water-borne sector, and the discharge of sludge from the tank is included in the solid-waste category.

Anaerobic biological processes are much more sensitive to quality variations in the wastewater than are the aerobic processes. Domestic septic tanks operate on a rather consistent type of household effluent and are not subject to the discharge of industrial wastes, which must be accommodated by most municipal plants and their digesters. When materials in concentrations that are toxic to the digestion process enter the digesters, the operating problems can be monumental[24].

Nitrogen compounds provide the buffering that is essential for effective digestion processes. Organic N is converted into ammonia, which with CO_2 and H_2O forms the buffer[25]:

$$CO_2 + H_2O + NH_3 \longrightarrow NH_4HCO_3 \qquad (7)$$

Because of the sensitivity of the anaerobic process and its comparatively slower reactions, aerobic sludge-digestion processes are being employed more and more.

The National Academy of Sciences estimates that 75 percent of the population is being served by central sewage-treatment plants[7]. This leaves 25 percent for septic tanks and digestion tanks. If 1.1 million metric tons of nitrogen a year were produced by the whole population, 0.84 million tons would be entering sewage treatment plants and 0.28 million tons would be entering septic-tank or individual systems. Of the 0.84 million tons entering sewage treatment plants, secondary treatment leaves about 3 kilograms of nitrogen per person per year in the discharge. Hence, by subtraction, 390 thousand metric tons of nitrogen would be entering sludge digestion processes yearly.

Anaerobic digester gases contain mostly CH_4, CO_2, and H_2O, with little degassing of nitrogen forms. Hence, the point-source discharge of nitrogen from sludge digestion tanks can also be estimated at approximately 390 thousand metric tons per year. Since septic tank systems give off the same gases as digestion tanks, the total output of nitrogen would again be somewhat equivalent to the input, a discharge of about 280 thousand metric tons per year.

Periodically, it is necessary to dispose of the accumulated sludge in septic tanks. This is generally accomplished by trucking it to a municipal sewage treatment plant, or by some type of controlled or uncontrolled ground disposal. The amount of nitrogen transferred is not likely to be very significant, even though the volume of septic-tank contents can be estimated at approximately one billion gallons per year (assuming five persons per septic tank, an average sludge capacity of 500 gallons per tank, and a cleaning once each five years).

In summary, the bulk of the nitrogenous materials discharged from septic tanks is percolated into the soil and ground water. The nitrogenous materials from municipal digesters enter the solid sphere, as defined herein.

URBAN RUNOFF

It once was acceptable practice to build "combined" sewer systems, ones that transport sewage to sewage treatment plants during dry weather and also drain the runoff from storms during wet weather. The excess flow (that which cannot be accommodated by the sewage treatment plant) of the "combined" sewage (sewage plus runoff) is diverted directly into surface water. The rationale behind this practice is that the increased flow of the streams during periods of rainfall could accommodate the oxygen demand due to the added increment of untreated, diluted sewage. Because of the widespread installation of combined systems in many major U. S. cities, much of the data in the literature concern the wastewater in such systems.

The earliest study about the quality of urban runoff *per se* reported by Public Health Service workers was from Moscow, Russia, in 1936[26]. Nitrogen information, however, was not reported. Later studies in the U. S. concerned catch-basin contents and samples from street gutters during rainfall. A 1954 English study noted that the first flush following a long dry period was particularly polluting; but, again, nitrogen information was lacking. The previously mentioned gutter samples plus studies in Sweden and South Africa have confirmed the high pollution loads that can be contributed by urban runoff, with organic N concentrations varying from 3.5 to 9.0 milligrams per liter.

Weibel, Anderson, and Woodard conducted a study of runoff from a residential-commercial area in Cincinnati, Ohio, in 1962-63. The mean N values expressed in mg/l observed in these studies were: NH_3-N, 0.6; organic N, 1.7; NO_3-N, 0.4; and NO_2-N, 0.05. Total N was calculated to be 8.9 pounds per year per acre[26].

In 1968, a study was conducted in the Detroit and Ann Arbor areas of Michigan[27]. The annual mean values observed given in milligrams per liter were: NH_3-N, 1; organic-N, 1; and NO_3-N, 1.5. Areal contributions for the three-month study expressed in pounds per acre were: NH_3-N, 0.7; organic N, 0.4; and NO_3-N, 0.8. Summing these and extrapolating on a straight-line basis, the yearly contribution per acre comes to 7.6 pounds, which is a reasonable check of the Cincinnati findings[7].

The Detroit-Ann Arbor study compared the quality of separately sewered storm water with combined sewer overflows on an areal basis. The extrapolated nitrogen data show that the combined sewer overflows produced 32 pounds of total nitrogen per acre per year, compared to the figure of 7.6 pounds for storm water alone. The workers observed that (1) the annual mean values for NH_3-N were more than ten times those observed in combined sewer systems; (2) that concentrations of organic N were fairly constant throughout the year; and (3) that the amount of NO_3-N dropped in the fall, which they attributed to a lower use of fertilizers at that time of year[27].

DeFilippi and Shih published a study of combined and separate systems in 1971[28]. They noted that the quality of storm sewage varied from storm to storm as well as within any single storm, and that this depended on the intensity and duration of rainfall, antecedent conditions, land use, topography, and flushing characteristics--among other factors. For their study of the District of Columbia, they utilized equipment that collected samples at five- or ten-minute intervals during the entire duration of storms. Each sample was analyzed. The only published information about nitrogen content was for total N--which ranged from 0.5 to 6.5 mg/l, with a mean of 2.1.

Comparing the means for total N of the three major studies shows:

	Mean amt. of total N (mg/l)
Cincinnati	2.75
Michigan	3.5
Washington, D. C. . . .	2.1

Runoff nitrogen discharges directly into waterways. Because of increased efforts to control water pollution, studies are underway in some areas to provide primary treatment for runoff waters. Chlorination is normally a health department requirement for application to such discharges; also, little is known about the chemical forms of nitrogen generated by the chlorination of organic N. Hence, it appears that much more study would be desirable before such plants come into wide use.

LANDFILL LEACHATE

A highly controlled study of the leachate from sanitary landfill has been under way by workers at Drexel University for a number of years[29]. A summary of the first two years of the study shows approximate values for total N (probably NH_3-N plus organic N) on a graph. As observed from that graph (approximate values only), total N peaked at about 490 mg/l within the first 20 days and then dropped sharply, varying from 15 to 80 mg/l for the next 130 days. Thereafter, the concentration ranged from 40 to a high of 210 milligrams per liter. An approximation for the two years might be about 90 milligrams per liter.

Very little leachate was produced initially. The first high total-N peak mentioned was related to the initial squeezing caused by compaction. A second peak coincided with the first leachate observed from water percolating through the fill. Once the system reached a water balance--with the water added equal to the leachate measured (at about 400 days), the total N also came into balance at about 110 milligrams per liter. Eliminating the water input decreased leachate production to zero.

A total of 421.5 gallons of water was added per year (according to average conditions of rainfall in southeastern Pennsylvania) to the landfill lysimeter of 36 square feet. The yearly contribution of TKN per square foot of landfill area averaged approximately 4 grams. This leachate exists in an anaerobic, hence in a reducing, environment; also, some losses of N_2 and NH_3 can be anticipated in such an environment. The Drexel studies demonstrated the presence of N_2 coming from the experimental unit, but the quantity was not reported. Once nitrogen is in an aerobic environment, oxidation to nitrate can be anticipated. The production of 4 grams per square foot per year of TKN is not unimportant. On an acreage basis, this amounts to 384 pounds per acre per year, compared to the previous contributions from urban runoff of 7 to 8 pounds. However, the acreages involved differed greatly.

SOLID WASTES

The two main types of these wastes emanating from the urban environment in a nonaerosol mode are sewage sludge and municipal refuse. Both have already been discussed from their water-borne aspects.

The disposal of sludge-digestion residues is usually governed by the economics of the individual sites. Some of the techniques being used are barging to sea (New York), ocean disposal through outfalls (California), dewatering and incineration (South Lake Tahoe), and land application (Chicago). Others include filling open mine pits, using lagoons, and hauling to sanitary landfills.

The estimated 390 thousand metric tons of digestion-tank nitrogen compares to 1.6 million metric tons of fertilizer N consumed in 1957[1]; and unless the sludge is used agriculturally, would appear to represent a considerable waste of this resource. The value of sludge in agricultural fertilization has long been known. Economically, however, it cannot compete with chemical fertilizers. The basic reason for this is the cost of removing the water. Sewage sludge is about 2 to 5 percent solids (95 to 98 percent water). The water represents a serious cost factor in terms of transportation.

Proprietary equipment is on the market that will achieve some dewatering. This equipment includes vacuum filters, centrifuges, and filter presses. Small sewage treatment plants generally dewater their sludges on drained, sand-drying beds. Before any wide-scale "solids to the land" program is undertaken, however, two significant factors must be reckoned with, and both concern health.

The first factor is that digestion does not destroy all of the potential pathogens in sewage sludge. Therefore, some means of treatment is needed in order to render the sludge nonpathogenic. One means could be heat. The second factor is the high concentration of heavy metals found in sludge[24].

Conceiveably, this might impose a severe limitation on the use of sludge. At the very least, more ought to be known about the ramifications.

An example of the type of effort needed can be illustrated using John, Van Laerhoven, and Chuah's recently published study about cadmium added to soils, versus plant uptake and phytotoxicity. They found that the cadmium in the plant tissue was related more to the amount of exchangeable cadmium in the soil than to the total amount of cadmium added to the soil. While greater soil acidity was associated with higher cadmium levels in plants, increased organic matter in the soil was related to lower plant cadmium. In other words, the organic matter added a capacity for adsorbing cadmium[30]. Since sewage sludge contains organic detritus, the use of sludge as a soil supplement may prevent the uptake of heavy metals by plants, even though these metals are present. On the other hand, the situation may be even more complex than is now apparent.

The movement of nitrogen into the soil from landfill operations can be stopped after the initial leaching due to compaction by providing a water-impermeable membrane cover over the landfill. Where the ground water levels are high enough to reach the fill, such an application is useless.

ANALYTICAL PROBLEMS

The traditionally important forms of nitrogen are ammonia, organic N, nitrite, and nitrate. All are customarily reported in terms of N, so values may be interpreted from one form to another without the use of a factor[2].

All nitrogen that exists as an ammonium ion or as ammonia is considered to be NH_3-N. It can be measured by direct Nesslerization or by distillation. Since the direct Nesslerization procedure is subject to serious error from extraneous color and turbidity, the distillation procedure is the one generally employed with wastewater. Because organic N is progressively ammonified by bacteria, the analysis is best conducted on a fresh sample. Storage is permissible if the sample is acidified with 0.8 milliliters of concentrated H_2SO_4 added to each liter of sample and stored at 4° Centigrade[31]. The percentage of relative error on six samples analyzed by distillation followed by a Nessler finish varied from 2 to 10 for up to 44 participating laboratories.

All nitrogen present in organic compounds is considered to be organic nitrogen. Most of the organic N in sewage is in the form of proteins or their degradation products: polypeptides and amino acids[2]. As with ammonia-N, the determination must be made on a freshly collected or specially preserved sample. The method fails to account for the N in azides, azines, azo, hydrazones, nitrate, nitrite, nitrile, nitro, nitroso, oximes, and semicarbazones. If ammonia is not first removed from the sample, the results are called TKN (the sum of NH_3-N and organic-N). At organic N concentrations of 0.8 and 1.5 mg/l, the percentage of relative error for 16 participating laboratories was 8.7 and 4, respectively[31]. The organic N procedure misses N compounds that are of considerable health importance.

Nitrite represents an intermediate state in the nitrogen cycle; and in "healthy" biological systems, its presence is a relatively fleeting one. Nitrite is sometimes used as a corrosion inhibitor in industrial process water, and care must be taken to prevent its entry into potable water systems through cross connections. Situations can be encountered in biological sewage-treatment processes in which nitrites will occasionally increase in concentration above their usual values. Since samples are subject to change with biological activity, analyses should be run only on fresh or quickly frozen samples. Acid preservation is acceptable with refrigeration. Nitrogen trichloride interferes, as do certain ions: antimonous, auric, bismuth, ferric, lead, mercurous, silver, chloroplatinate, and metavanadate. The percentage of relative error was 12 for 49 laboratories analyzing a prepared sample containing 0.25 milligrams per liter[31].

Standard Methods[31] offers tentative procedures, but recommends no particular one for the determination of nitrates in wastewater, which Sawyer indicates is the most difficult work an analyst has to perform in order to obtain results in which he can be genuinely confident[2]. Each of the procedures has objectionable interferences, which the analyst must consider in selecting a procedure. All tests must be run on freshly collected or specifically preserved samples. A summary of the percentage of relative errors follows[31]:

Procedure	No. of labs	NO_3 (mg/1)	Pct. of relative error (mg/1)
Zinc reduction	..	1.4	+0.2
Cadmium reduction	11	50	47.3
Brucine	50	50	7.6
Phenoldisulfonic acid	46	1	31 to 38
Chromotropic acid	32	50	12.5

As Sawyer saws, "The need is great for a more refined and exact method of analysis"[2].

CONCLUSIONS AND SUGGESTIONS

Some 202 million Americans produce an estimated 1.1 million metric tons of nitrogen a year. Of this, an estimated 0.84 million tons enter sewage treatment plants. The remaining 0.28 million tons go into septic tanks or individual systems. Of the 0.84 million metric tons entering sewage treatment plants, effluents are estimated to discharge 3 kilograms of nitrogen per person per year, or 0.45 million tons. The form of the nitrogen discharged (the relative mix of ammonia, organic, and nitrate forms of nitrogen) differs widely from plant to plant Each form, however, produces undesirable environmental effects. Additionally, all of them will ultimately oxidize to the stable, soluble-nitrate form in an oxidizing environment.

To obtain some perspective about the enormity of the nitrogen problem, one needs only to look at its theoretical impact in terms of drinking water standards. Of the total annual precipitation on the U.S., an estimated 100 million acre-feet are diverted and consumed[32]. The 0.45 million metric tons of nitrogen discharged from sewage treatment plants yearly is sufficient to raise 12 trillion gallons of water to the limit of 10 mg/l of nitrate nitrogen specified by Drinking Water Standards. The result in terms of undesirable nutrient levels would be even more severe.

The trend in sewage treatment over the past two decades--with the exception of the application of extended aeration plants and until the adoption of water quality standards--was to increasingly ignore the nitrogenous aspects of sewage treatment, much to the dismay of officials concerned with water supply and purification. Within the past several years, however, the federal water pollution control program has been oriented more and more toward nutrient limitations.

Control considerations involve the analytical area. Problems are pronounced in the application of the BOD test in a meaningful way, in determining nitrates with confidence, in knowing what chemical species comprise the 20 percent of undetermined N of the TKN procedure, and in knowing what chemical forms of nitrogen are created by chlorinating the undetermined nitrogen.

The following suggestions are given (with explanatory information inserted):

1. A national policy concerning nitrogen control should be developed, one that would result in greater nitrogen removals by sewage treatment plants.
2. Research relative to nitrogen removal needs to be greatly expanded.
3. More effort should be directed toward developing an improved nitrate nitrogen procedure for use on polluted waters, including sewage.
4. The chemical forms of nitrogen that make up the 20 percent of unaccounted-for N or TKN, as revealed by Hanson and Lee[2], should be identified.
5. Study of the chemical forms of nitrogen created by chlorinating the undetermined N in TKN should be initiated.
6. The BOD test should be modified to reflect only the carbonaceous aspect, and should be supplemented by the four nitrogen determinations of

environmental significance--the ammonia, organic, nitrite, and nitrate forms of nitrogen--for the routine monitoring of our nation's sewage treatment plants.

7. Studies should be undertaken to quantify the chemical forms of nitrogen that are not measured by conventional analysis.

Individual sewage systems discharge into ground water. These systems process an estimated 0.28 million metric tons of nitrogen yearly. Some of this nitrogen is taken up by plants. Yet, the magnitude of this discharge comes into perspective when one realizes that 0.28 million metric tons of nitrogen is sufficient to raise 7.4 trillion gallons of water to the 10 mg/l limit specified by Federal Drinking Water Standards. Individual systems manifest problems (other than inherent ones) only when they are improperly located or when their density is too high. Where problems do appear, several alternatives are available; hence, these suggestions:

8. Regulations should be enacted by all states to limit the density of individual sewage-disposal systems.

9. Where ground water is already affected, Federal money should be made available to the communities or areas involved, in order to speed up the delivery of an uncontaminated supply.

10. Where alternate sources of water are not available, high priority should be given to affected communities for the construction of sewers and sewage treatment plants.

Urban runoff contributes substantially to environmental nitrogen. It is not feasible to adopt biological processes to control this problem. Certainly, however, chemical-physical treatment can bring about some improvement; thus, the next two suggestions:

11. All storm-water treatment plants currently in operation or under construction should be set up to monitor routinely for nitrogenous materials.

12. The desirability of chlorinating storm-water plant effluents should be evaluated from the viewpoint of what chlorinated products are formed when this is done.

Landfill leachate imposes massive nitrogen loads calculated at some 384 pounds per acre per year on contiguous ground and surface water. Other than the initial peak caused by compaction, eliminating the water input through the fill decreases leachate production to zero; therefore, these suggestions are also given:

13. Where sanitary landfills are not in continuous contact with ground water, a water-impermeable membrane should be incorporated in or on top of the fill.

14. Where landfills must be immersed in ground water, other solid-waste disposal techniques should be employed.

The disposal of sewage sludges is estimated to include 390 thousand metric tons of nitrogen yearly, a substantial waste when not applied usefully. Research is needed to achieve more economic dewatering and pathogen destruction. Additionally, greater knowledge is needed about the mobility of heavy metals; hence, these three suggestions:

15. The technology of dewatering sewage sludge should be developed further.

16. More research should be devoted to the means of destroying pathogens in sludge.

17. Studies of the agricultural use of sewage sludge should be expanded, with a significant increase in the attention paid to heavy metals and to a better understanding of their movement and concentration.

REFERENCES

1. Task Group Report, Sources of nitrogen and phosphorus in water supplies. *Jour. Am. Water Works Assn.* 59:3, p. 344 (1967).

2. Sawyer, C.N. *Chemistry for Sanitary Engineers*. McGraw-Hill Book Co., Inc., p. 289, New York City (1960).

3. Environmental Protection Agency. *Nitrogen Supersaturation in the Columbia and Snake Rivers*. Technical Report No. TS 09-70-208-016.1, Office of Water Programs, Region X, Seattle, Washington (July 1971).

4. Carlson, A.J., and Johnson, V. *The Machinery of the Body*, p. 335. University of Chicago Press (1937).

5. Hanson, A.M., and Lee, G.F. Forms of organic nitrogen in domestic wastewater. *J. Water Pollution Control Fed.* 43:11, p. 2,271-79 (November 1971).

6. Fruton, J.S., and Simmonds, S. *General Biochemistry*, 2nd ed. Wiley and Sons, Inc. New York City (1961).

7. Committee Report. *Accumulation of Nitrate*, National Academy of Sciences, Washington, D.C. (1972).

8. Symons, J.M. Urban sources of nitrates. Proceedings, Twelfth Sanitary Engineering Conference, Nitrate and Water Supply: Source and Control, University of Illinois at Urbana-Champaign (February 11, 12, 1970).

9. Committee Report. Standard practice in separate sludge digestion. *Proc. Am. Soc. Civ. Engr.* 63:39 (1937).

10. Weibel, S.R. Urban drainage as a factor in eutrophication. In *Eutrophication: Causes, Consequences, Correctives*, p. 388. National Academy of Sciences, Washington, D.C. (1969).

11. Keup, L.E., and Mackenthun, K.M. Lakes-restoration and preservation. *Water and Sewage Works* 117, R16, 21 (November 1970).

12. Reeves, T. G. Nitrogen removal: A literature review. *Jour. Water Pollution Control Fed.* 44:10, p. 1,895-1,908 (October 1972).

13. U.S. Dept. of Health, Education, and Welfare. *Interaction of Heavy Metals and Biological Sewage Treatment Processes.* Public Health Service Publication 999-WP-22, Cincinnati, Ohio (1965).

14. Busch, A.W. *Aerobic Biological Treatment of Waste Waters*, p. 170. Oligodynamics Press, Houston, Texas (1971).

15. U.S. Department of the Interior. *Report of the National Technical Advisory Committee.* Federal Water Pollution Control Administration, Washington, D.C. (April 1, 1968).

16. *Water Newsletter*. Water Information Center, Inc. 14:21 (November 6, 1972).

17. St. Amant, P.P., and McCarty, P.C. Treatment of high nitrate waters. *Jour. Am. Water Works Assn.* 61, p. 659 (December 1969).

18. Parkhurst, J.D., *et al.* Pomona activated carbon pilot plant. *Jour. Water Pollution Control Fed.* 39:10, part 2, R70-R81 (October 1967).

19. *Summary Report, Jan. 1962--June 1964, Advanced Waste Treatment Research*, AWTR-14, Public Health Service Publication No. 999-WP-24 (April 1965).

20. Culp, R.L., and Culp, G.L. *Advanced Wastewater Treatment*. Van Nostrand Reinhold Co., New York City (1971).

21. Zuckerman, M.M., and Molof, A.H. High quality reuse water by chemical-physical wastewater treatment. *Jour. Water Pollution Control Fed.* 42, 437 (March 1970).

22. Bishop, D.F., *et al.* Advanced waste treatment systems at the Environmental Protection Agency--District of Columbia pilot plant. Paper presented at the *68th National Meeting of the American Institute of Chemical Engineers*, Houston, Texas (March 1971).

23. Pressley, T.A., Bishop, D.F., and Roan, S.G. Nitrogen removal by breakpoint chlorination. Robt. A. Taft Water Research Center, Cincinnati, Ohio (September 1970).

24. Regan, T.M., and Peters, M.M. Heavy metals in digesters: Failure and cure. *J. Water Pollution Control Fed.* 42:10, p. 1832 (October 1970).

25. Mohanrao, G.J., Sastry, C.A., and Mehta, R.S. Fundamentals of anaerobic digestion. *Environmental Health* 5:2, p. 169 (April 1963).

26. Weibel, S.R., Anderson, R.D., and Woodward, R.L. Urban land run-off as a factor in stream pollution. *J. Water Pollution Control Fed.* 36:7, p. 914 (July 1964).

27. Burm, R.J., Krawczyk, D.F., and Harlow, G.L. Chemical and physical comparison of combined and separate sewer discharges. *J. Water Pollution Control Fed.* 40:1, p. 112 (Jan. 1968).

28. DeFilippi, J.A. and Shih, C.S. Characteristics of separated storm and combined sewer flows. *J. Water Pollution Control Fed.* 43:10 (October, 1971).

29. Fungaroli, A.A., and Steiner, R.L. Laboratory study of the behavior of a sanitary landfill. *J. Water Pollution Control Fed.* 43:2, p. 252 (February 1971).

30. John, M.K., Van Laerhoven, C.J., and Chuah, H.H. Factors affecting plant uptake and phytotoxicity of cadmium added to soils. *Environ. Science and Tech.* 6:12, p. 1,005-1,009 (November, 1972).

31. American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*, 13th ed. New York City (1971).

32. Office of Science and Technology. *A Ten-Year Program of Federal Water Resources Research*, p. 4. Supt. of Documents, U.S. Govt. Print. Office,

Washington, D.C. 20402 (February 1966).

33. Young, James C. Chemical methods for nitrification control. *J. Water Pollution Control* 45:4, p. 637-646 (April 1973).

Discharges into the Atmosphere

Sources of Nitrogenous Compounds and Methods of Control

JAMES N. PITTS, JR. AND ALAN C. LLOYD

FOR KEY NITROGENOUS MATERIALS IN THE LOWER ATMOSPHERE (the troposphere), we review here the concentrations, sources, sinks, transformations, and the health and environmental effects. Both natural and anthropogenic sources are considered, as are those nitrogenous compounds that are known (or believed) to play significant roles in the natural and polluted troposphere. Those compounds include the inorganic gases--nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrous and nitric acid (HONO and HNO_3), and ammonia (NH_3); the inorganic particulates--nitrites (NO_2^-), nitrates (NO_3^-), and ammonia salts (NH_4^+), and the organic peroxynitrates--such as peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBzN). Others that may play important roles in photochemical smog such as NO_3 and N_2O_5 are treated in detail in the reviews referenced herein, and are beyond the scope of this paper.

This is not a literature survey; rather, it is a brief yet critical examination of existing information. When a number of references apply to the same data, only the most recent are generally given. Recent, detailed, and relevant reviews include those of Schuck and Stephens, 1969; Stephens, 1969; Altshuller and Bufalini, 1971; Air Quality Criteria for Nitrogen Oxides, 1971; Stern, 1968; Calvert, Demerjian, and Kerr, 1972; Demerjian, Kerr, and Calvert, 1973; Robinson and Robbins, 1972; Niki, Daby, and Weinstock, 1972; and Levy, 1973.

ATMOSPHERIC CONCENTRATIONS AND SOURCES

NITRIC OXIDE AND NITROGEN DIOXIDE

Historically, the *sum* of the concentrations of nitric oxide and nitrogen dioxide (NO_x) has been used in referring to the concentrations of nitrogen oxides in polluted atmospheres. This came about because the Jacobs-Hochheiser

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analytical method, which employs a colorimetric determination of nitrogen dioxide as an azo dye, does not give the individual concentrations of nitric oxide and nitrogen dioxide. That is unfortunate because the two species have vastly different physical, chemical, and biological properties. For example, NO is colorless and relatively nontoxic; but NO_2 is a deep red-brown, is toxic, and is the major precursor to ozone in smog.

The recent introduction of chemiluminescent analytical methods specific to nitric oxide will rectify this situation. They are based on the reaction

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (1)$$

in which the NO_2^* is an electronically excited state that emits intense visible light. Reaction is also of great interest in the SST debate. Johnston (1971) has suggested it as a process that could lead to a serious depletion of ozone in the stratosphere if large amounts of NO are emitted there by jet aircraft engines.

Robinson and Robbins (1972) suggest that NO formed by bacterial action, and subsequently oxidized into NO_2, could produce the NO_2 levels of about 7 parts per million measured in rural areas of North Carolina by Ripperton *et al.* (1970).

The remaining sources of atmospheric NO_x are due to man-made pollution resulting from high-temperature combustion process involving air. The reactions are complex, but the overall equilibrium can be represented as

$$N_2 + O_2 \rightarrow 2NO; \quad \Delta H = 43 \text{ kcal/mole} \qquad (2)$$

Since the overall reaction is strongly endothermic, relatively small increases in the reaction temperature during combustion greatly favor NO production.

In typical, high-efficiency combustion systems (such as fossil-fuel power plants and internal-combustion automobile engines) approximately 95 percent of the NO_x is emitted as NO; the remainder as NO_2. In polluted atmospheres, the NO is then oxidized into NO_2 by two distinct mechanisms. At relatively high concentrations of NO (1,000 to 2,000 parts per million), it is thermal.

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

At low ambient levels (0.5 ppm), it is photochemical (see the section on atmospheric transformations and sinks).

$$NO + \text{Hydrocarbons} + \text{Solar UV} \rightarrow NO_2 + O_3 + \text{other compounds} \qquad (4)$$

Controls are being installed on automobiles and emissions from stationary sources are being curtailed; therefore, the contribution of NO_x from such sources as aircraft and domestic home heaters will become increasingly important. Recently, the suggestion has been made that atmospheric nuclear tests are sources of NO_x; but fortunately, these have been relatively isolated occurrences (Foley and Ruderman, 1972).

From the data tabulated by Robinson and Robbins (1972) and the measurement of Ripperton *et al.* (1970), the levels of NO and NO_2 in relatively *unpolluted* environments fall within the ranges of about 1 to 3 and 1 to 5 ppb, respectively. In urban air, however, these levels increase significantly. In smoggy Los Angeles air, for example, the values for [illegible] NO_2 are typically 0.1 to 1.5 ppm and 0.05 to 0.3 ppm, respectively.

NITROUS OXIDE

This is the most abundant, *naturally* occurring oxide of nitrogen. Ambient concentrations in nonpolluted air are typically between 0.25 and 0.5 ppm (Cadle and Allen, 1970: Robinson and Robbins, 1972).

The major source of N_2O is evolution from the soil as the result of the decomposition of nitrogen compounds by soil bacteria. Arnold (1959) verified this by showing that N_2O was produced by bacterial action on ammonia and nitrate salts. The possibility that some N_2O could be produced from the oceans should not be ruled out (Junge and Hahn, 1971).

In terms of anthropogenic sources, there is some evidence that N_2O may be a product from certain catalytic devices proposed for use on automobiles to meet the 1975-76 Federal Emission Standards. It is too soon to realistically consider the consequences of this possible source, but they could be significant in both the upper and the lower atmosphere.

NITROUS AND NITRIC ACIDS

Preliminary measurements indicate that nitric acid is present in trace amounts (measured in ppb) in ambient photochemical smog (Price and Stephens, 1971). No determination has been made in the normal troposphere, but Levy (1973) has predicted values as high as 30 parts per billion. The main formation reaction is generally assumed to be

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{5}$$

A possible heterogenous path also exists.

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{6}$$

Likewise, nitrous acid may well be formed in the atmosphere by the reactions

$$NO + NO_2 + H_2O \rightleftarrows 2HONO \tag{7}$$

$$OH + NO + M \rightarrow HONO + M \tag{8}$$

Nitrous acid has not yet been measured in ambient air, although some researchers think it may play a significant role in the formation of photochemical smog (Johnston, 1970; Demerjian, Kerr, and Calvert, 1972 and 1973).

It is interesting to note that nitric acid has been detected in the stratosphere at a maximum concentration of $\sim 1 \times 10^{10}$ molecules cm^{-3} at $\sim(19 \pm 5)$ km (Williams *et al.*, 1972; Lazrus *et al.*, 1972).

AMMONIA

The major source of ammonia is the bacterial breakdown of amino acids in organic waste material (Altshuller, 1958; Junge, 1963; Robinson and Robbins, 1972). However, Junge (1963) states that both the soils and the oceans can act as sources as well as sinks, depending on conditions.

Anthropogenic sources of ammonia are not as significant as the ones just given. Yet, when coal and oil are burned, measurable quantities of ammonia are emitted. Further, the catalyst systems proposed for automobiles so they will meet the 1975-76 Federal Air Quality Standards could become additional sources of ammonia formed by the reaction below (Klimisch and Taylor, 1973).

$$5H_2 + 2NO \rightarrow 2NH_3 + 2H_2O \qquad (9)$$

As has been noted, the atmospheric concentration of ammonia depends on biological activity; but the background level is around 6 ppb (Robinson and Robbins, 1972). Measured concentrations have ranged from about 1 ppb (Junge, 1963) to over 20 ppb (Lodge and Pate, 1966).

PAN AND PBzN

Very little data are available about the atmospheric concentrations of these compounds on a global basis. Although peroxybenzoyl nitrate has been identified in chamber experiments, it has not yet been detected in the atmosphere. The peroxyacyl nitrates are products of photochemical reactions in polluted atmospheres, involving olefins and NO_2 as well as other precursors (Stephens, 1969). No natural sources are known.

The concentrations of peroxyacyl nitrates in ambient smog within the Los Angeles Basin are between 0.005 and 0.05 parts per million. PAN is a powerful lachrymator, causing damage to susceptible plants at concentrations of greater than 0.01 ppm; and it may well have more serious and lasting effects on man.

PARTICULATE NITROGENOUS MATERIAL

Atmospheric nitrogenous aerosols may be formed by the reaction of NO_2 and NH_3 to give compounds containing NO_2^-, NO_3^-, and NH_4^-. One of the most common compounds identified in aerosol analysis is $(NH_4)_2SO_4$.

Few data are available on the concentration of nitrate or ammonium in aerosols; but generally, the particulate ions are more dilute than the gaseous fractions of NO_2 and NH_3 (Robinson and Robbins, 1972). Lodge *et al.* (1960) found nitrate concentrations of about 0.015 micrograms per cubic meter in the mid-Pacific area, while Junge (1956) measured NO_3^- and NH_4^+ concentrations of 0.08 and 0.04 $\mu g/m^3$, respectively, for Hawaii and average NO_3^- levels of about 0.33 $\mu g/m^3$ for Florida.

ATMOSPHERIC TRANSFORMATIONS AND SINKS

NITROGEN OXIDES

There are two major mechanisms for the conversion of NO into NO_2 in the troposphere. The thermal reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{3}$$

is slow in ambient air, because the reaction rate depends on the square of the nitric oxide concentration. However, the reaction is considerably faster in such things as the plumes of fossil-fuel power plants, where concentrations of 1,000 ppm and more are often encountered.

In simulated atmospheres containing only NO_x and air and irradiated with ultraviolet light, the NO_2 photolyses to produce oxygen atoms which, in turn, result in the formation of ozone when the NO levels become very small.

$$NO_2 + h\nu\ (2950\ \text{Å} - 4200\ \text{Å}) \rightarrow NO + O(^3P) \tag{10}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{11}$$

$$O_3 + NO \rightarrow O_2 + NO_2^* \qquad (1)$$

The net effect of irradiation on this strictly *inorganic* system is to set up a dynamic equilibrium that results in a low overall production of O_3:

$$NO_2 + O_2 \overset{h\nu}{\rightarrow} NO + O_3 \qquad (5)$$

However, when hydrocarbons or oxygenated hydrocarbons are present, which is the case in polluted atmospheres, this dynamic equilibrium is unbalanced. The imbalance is particularly rapid if an olefin or an alkylated benzene is used (both of which are common constituents of gasoline), and the following events take place:

1. The hydrocarbons are oxidized and disappear.
2. Reaction products, such as aldehydes, nitrates, PAN, and others, are formed.
3. Nitric oxide (NO) is rapidly converted into nitrogen dioxide (NO_2).
4. When all of the NO has been used up, substantial amounts of O_3 begin to appear. On the other hand, PAN and the aldehydes are formed from the beginning of the reaction.

The full details of the mechanism are still not known, as pointed out in recent reviews (Altshuller and Bufalini, 1971; Niki, Daby, and Weinstock, 1972; Demerjian, Kerr, and Calvert, 1973). These reviews adequately cover the known details of the mechanism. Here, we will concentrate on some of the more recent developments relating to the oxidation of nitric oxide.

The hydroxyl radical is now thought to be the main chain carrier in photochemical smog (Demerjian, Kerr, and Calvert, 1972). It is interesting that it was as late as 1969 that OH was first suggested to play a significant role in the mechanism of photochemical smog formation (Westberg, Cohen, and Wilson, 1971; Niki, Daby, and Weinstock, 1972; Stedman *et al.*, 1970; Heicklen, Westberg, and Cohen, 1971; Weinstock, Daby, and Niki, 1971):

$$HO + CO \rightarrow H + CO_2 \tag{12}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{13}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{14}$$

Recent data have shown that the oxidation of NO by Reaction 14 is rapid (Davis *et al.*, 1973).

For almost fifteen years, the general assumption was that Reaction 15, where R is an alkyl group, was rapid and was a key process in the oxidation of NO into NO_2 in photochemical smog.

$$RO_2 + NO \rightarrow NO_2 + RO \tag{15}$$

However, Spicer, Villa, Wiebe, and Heicklen (1973), on the basis of their experiments using methylperoxy radicals, CH_3O_2, have stated flatly that this oxidation does *not* occur and, consequently, that it should be omitted from the generally accepted mechanisms for photochemical smog formation. However, these results are difficult to reconcile with (1) the fast rate of the somewhat analogous oxidation with HO_2, Reaction 14; (2) the 7 kcal/mole greater exothermicity of Reaction 15 over Reaction 14 for $R = CH_3$; and (3) the generally accepted necessity of incorporating Reaction 15 into the development of photochemical smog mechanisms (Altshuller and Bufalini, 1971; Niki, Daby, and Weinstock, 1972; Demerjian, Kerr, and Calvert, 1973). Clearly, further studies of this key oxidation step are required.

Other atmospheric transformations include the oxidation of NO by peroxyacetyl nitrate (PAN) (Schuck and Stephens, 1969) and by free radical species, such as NO_3 and RO_3 (Demerjian, Kerr, and Calvert, 1973). Nitrous acid may also be formed by one of the removal processes for NO_x:

$$NO_2 + NO + H_2O \rightarrow 2HONO \tag{7}$$

Nitrogen dioxide catalyzes the isomerization of olefins in the gas phase, although the reaction rates under ambient conditions are probably too small to make such reactions significant in the chemistry of urban atmospheres (Sprung, Akimoto, and Pitts, 1971; Akimoto, Sprung, and Pitts, 1972).

NITROUS OXIDE, N_2O

In typical gas-phase reactions at room temperature, nitrous oxide is generally considered to be quite inert, chemically. Thus, it has always been assumed to be of little importance in tropospheric reactions. To date, there is no experimental evidence that it is significantly involved in photochemical smog formation. However, this view should be accepted with some reservation because N_2O is, in fact, an excellent source of oxygen atoms. It may well be an unsuspected oxidant in tropospheric systems, although this is only an "educated hunch."

Photodissociation of N_2O proceeds by two routes--direct photolysis at wavelengths around 2000 Å, Process 16, and mercury photosensitization at 2537 Å, Reaction 17:

$$N_2O + h\nu \longrightarrow N_2 + O(^1D) \tag{16}$$

$$N_2O + Hg(g) + h\nu \xrightarrow[\lambda=2537\ \text{Å}]{} N_2 + O(^3P) \tag{17}$$

Nitrous oxide does react with $O(^1D)$:

$$N_2O + O(^1D) \longrightarrow NO + NO \tag{18}$$

$$\longrightarrow N_2 + O_2 \tag{19}$$

But since the concentration of these electronically excited oxygen atoms is extremely small in the troposphere (Levy, 1973), Reactions 18 and 19 are not important loss mechanisms. They assume far more importance in the stratosphere, the major sink for N_2O. Thus, N_2O is transported vertically where it mainly undergoes photodissociation, but also reacts with $O(^1D)$ atoms

(McElroy and McConnell, 1971), since they are present in much larger concentrations in the stratosphere than in the troposphere.

It is interesting to note that Schultz, Junge, *et al.* (1970) suggest that the tropospheric lifetime of N_2O may be ten years or less. This is much smaller than the value of seventy years calculated by Bates and Hays (1967), and may be indicative of the fact that N_2O does undergo tropospheric reactions that have not yet been identified.

NITROUS AND NITRIC ACIDS

There are two main mechanisms for the formation of nitrous acid in the atmosphere:

$$NO + NO_2 + H_2O \rightarrow 2HONO \qquad (20)$$

$$OH + NO + M \rightarrow HONO + M \qquad (21)$$

Stuhl and Niki (1972) have studied Reaction 21. They found that at 1 atmosphere, it is in its second-order regime and has a bimolecular rate constant of about 1×10^9 l mole^{-1}s^{-1}. The fast rate could make this a significant atmospheric formation reaction for HONO, particularly in the dark, when the facile photolytic decomposition reaction below does not occur.

$$HONO + h\nu\ (\lambda < 4000\ \text{Å}) \rightarrow HO + NO \qquad (22)$$

The latter photolysis is the main sink for nitrous acid, as well as being the main reason for the observation by Demerjian, Kerr, and Calvert (1972 and 1973) that HNO_2 can increase the initial rate of smog-forming reactions.

The major gas-phase formation reaction for nitric acid is

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (23)$$

This reaction is a rapid one; and under atmospheric conditions, should display second-order kinetics (Simonaitis and Heicklen, 1972; Anderson and Kaufman, 1972; Morley and Smith, 1972; Westenberg and de Haas, 1972).

Simonaitis and Heicklen reported a second-order rate constant of approximately 10^9 l mole^{-1}s^{-1} in reasonable agreement with the value given by Morley and Smith.

Nitric acid is formed by the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (24)$$

This is believed to occur heterogeneously, since the gas-phase reaction is very low (Levy, 1973).

The ultraviolet absorption spectrum of nitric acid has been determined by Johnston and Graham (1973), and has been found to extend significantly into the actinic ultraviolet to about 3,200 Å. It is believed to undergo photolysis in the atmosphere to produce the highly reactive species OH, with a quantum yield as yet undetermined. From the continuous nature of the absorption spectrum, it would appear to photodissociate with reasonable efficiency.

$$HNO_3 + h\nu\ (\lambda < 3{,}200\ \text{Å}) \rightarrow OH + NO_2 \qquad (25)$$

Little information is available on the gas-phase atmospheric reactions of HNO_3. Recent measurements of the reaction

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (26)$$

by Morley and Smith (1972) indicate that this reaction could be important in both the polluted and unpolluted troposphere. The rate constant was given as about 10^8 l mole^{-1}s^{-1}. Although no measurements have been reported, the analogous reaction for nitrous acid

$$OH + HNO_2 \rightarrow H_2O + NO_2 \qquad (27)$$

could also occur at a significant rate (Demerjian, Kerr, and Calvert, 1973).

Reactions with other radical species could occur for both these compounds, although the highly reactive hydroxyl radical is almost certainly the most important. Finally, reactions with particulates and wash-out mechanisms are likely to be significant removal mechanisms for atmospheric nitric acid.

AMMONIA

Ammonia undergoes a rapid reaction with acid

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (28)$$

The reaction probably occurs via a heterogeneous mechanism. The reaction with ozone is likely to be unimportant (Cadle and Allen, 1970).

Ammonia also reacts with oxygen atoms and with hydroxyl radicals

$$NH_3 + O \rightarrow NH_2 + OH \qquad (29)$$

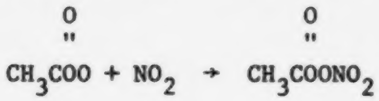
$$NH_3 + OH \rightarrow NH_2 + H_2O \qquad (30)$$

The respective rate constants are 1×10^6 l $mole^{-1}s^{-1}$ (Wong and Potter, 1963) and about 1×10^8 l $mole^{-1}s^{-1}$ (Stuhl and Niki, 1972). The rapid rate of Reaction 30 suggests that it could be a significant sink for atmospheric ammonia. However, the main sink is likely to be the reactions with acids already mentioned to produce aerosols.

Ammonia does not absorb at wavelengths exceeding 2,200 Å and, consequently, does not undergo direct photolysis or excitation in the troposphere.

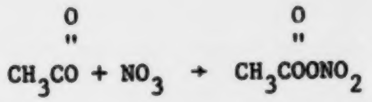
PAN AND PBzN

The complete mechanism for the formation of PAN has not been fully determined, although Stephens (1969) thinks the final step is:



$$CH_3\overset{O}{\overset{\|}{C}}OO + NO_2 \rightarrow CH_3\overset{O}{\overset{\|}{C}}OONO_2$$

However, Hanst (1971) has suggested that a possible alternative or parallel reaction is



$$CH_3\overset{\overset{O}{\|}}{C}O + NO_3 \rightarrow CH_3\overset{\overset{O}{\|}}{C}OONO_2$$

Further work is required in order to fully understand the relative merits of the two mechanisms.

PAN oxidizes nitric oxide in the gas phase to nitrogen dioxide at a rate that makes the reaction of potential significance in the conversion of NO into NO_x in polluted atmospheres (Schuck and Stephens, 1969; Schuck, Stephens, and Price, 1972).

Although PBZn has yet to be observed in the atmosphere, it is expected to also act as an effective oxidizing agent for NO, even though the rate of oxidation may be slow because of the very small concentration (1 to 5 ppb) expected to be present in polluted atmospheres (Stephens, 1972). PAN does not significantly absorb the solar radiation present in the lower atmosphere, and it is difficult to obtain actual estimates of the maximum rate of photolysis in ambient air (Stephens, 1969). Decomposition on surfaces or on aerosol particles could be one of the sinks for PAN in the atmosphere, since it has a low but erratic stability.

PARTICULATES

This is such a broad and complex area that it cannot be covered adequately here. Detailed discussions have been given in two recent publications--"Air Quality Criteria for Particulate Matter" (PHS, National Air Pollution Control Association, 1969), and "Aerosols and Atmospheric Chemistry" (G.M. Hidy, Editor, Academic Press, N.Y., 1972). Only a few examples will be given.

Nitrate aerosols represent the final stage in the atmospheric oxidation of gaseous NO_x. Thus, according to Hidy and Friedlander (1971), nitrate particulates are formed from the large natural emissions of NO and NO_2 into the atmosphere. Substantial quantities of particulate nitrates are also formed in all urban areas affected by photochemical smog. Thus, the atmospheric burden of particulate nitrates has become increasingly important since the levels of NO_x have increased dramatically in urban regions throughout the U.S. during the last few years.

Two mechanisms are suggested by Hidy and Friedlander for the formation of particulate nitrate in the Los Angeles Basin.

1. The reaction between NO_2 and NaCl, the latter being present in particulate matter originating from the ocean.
2. Photochemical reactions involving NO_2 and hydrocarbon vapors.

Particle-gas and particle-particle reactions can occur, but the latter have received even less study than the former. Particle-particle reactions are likely to occur in the size range below 1 micron.

The reaction between sulfuric acid and ammonia that produces $(NH_4)_2SO_4$ was studied by Robbins and Cadle (1958). Their results helped to show some of the effects of humidity on aerosol production.

The chief removal processes for particulate matter are the:

1. Coagulation of smaller particles to produce fallout.
2. Natural deposition of particles.
3. Washout processes in which the air is "scrubbed," for example, by rain.

In conclusion, the degree of sophistication in modeling the chemistry of urban atmospheres is far from the stage in which heterogeneous reactions involving particulates can be incorporated into the mechanisms. Much more work needs to be carried out, both on the modeling aspects and in the chemistry and physics of atmospheric particulate matter.

CONTROL MEASURES

There are two general approaches to controlling the oxides of nitrogen: (1) modifying the combustion process in such a way as to *in situ* reduce the nitric oxide formation; and (2) removing nitrogen oxides in the effluent exhaust gases by physical or chemical methods. These are discussed in detail in the EPA document on the Control of NO_x from Stationary Sources, in "Control Techniques for CO, NO_x and Hydrocarbon Emissions from Mobile Sources" (NAPCA 1970) and in Stern (1968); also, these approaches have been reviewed recently by Bagg (1971).

STATIONARY SOURCES

Several means are currently employed to reduce the formation of NO_x during the combustion process in large-scale burners, such as those associated with fossil-fuel power plants.

The first involves redesigning the original combustion source and includes a two-stage combustion process and tangential instead of horizontal firing. Tangential firing might reduce NO_x levels by as much as 50 per cent. Similar and perhaps even more effective controls can be achieved by two-stage combustion (Bagg, 1971).

The second general *in situ* approach for NO_x control in stationary sources involves changing the chemistry of the combustion process by changing the fuel or by introducing fuel additives. The former is relatively straightforward approach--the order of *decreasing* NO_x emissions being coal, fuel oil, and natural gas. For example, a switch from fuel oil to gas may reduce NO_x emissions by 50 percent. A major problem is the current and rapidly growing shortage of natural gas in the U.S. The issue clearly involves a complex, sensitive set of priorities dealing with considerations of ecology versus economics, and directly involving the public, legislators, control agencies, and industry.

Several techniques are employed to remove NO_x from exhaust gases following combustion. These include, for example, catalytic reduction and sorption in solutions or on solids such as molecular sieves or silica gel (NAPCA Control Document, 1970; Stern, 1968; Bagg, 1971). Sorption techniques, although attractive for small volumes of exhaust gases, are presently uneconomical for large-scale combustion units. Catalytic conversion is more attractive; and in the case of removing NO_x in the tail-gas from nitric acid plants, platinum metals have been proven to be quite effective, with up to a 90-percent removal of NO_x reported (Anderson *et al.*, 1961).

Again, we should note that multiple-point sources such as domestic home heaters also contribute substantially to the atmospheric NO_x burden and that control measures for such small individual units may well be necessary in the not-too-distant future.

MOBILE SOURCES

The major mobile source of NO_x is the motor vehicle, but it is significant that emissions from such jet aircraft engine have risen dramatically as new and more powerful models have been introduced during the last fifteen years. This fact, plus the greatly expanding fleets of new jumbo jets and booming air-traffic business, make jet aircraft engines a potentially serious source of NO_x, one that is already significant in all modern cities.

Several methods are employed to reduce NO_x emissions on automobile engines. A summary follows.

Retrofit systems for used cars. These include such alterations as changing the timing by a "vacuum spark disconnect" device and exhaust-gas recirculation (EGR). Both devices are accredited for installation in California cars, 1966 through 1970, which are notoriously high emitters of NO_x. Unfortunately, the control strategy for CO and hydrocarbons has resulted in combustion conditions more favorable to NO_x formation.

New engine systems. The 1970 Muskie Amendment to the National Clean Air Act set strict controls for 1975 and 1976 for the emissions of hydrocarbons, CO and NO_x. The controls are identical for hydrocarbons and CO for both years, but in 1976 they are very much tighter for NO_x than in 1975. The chief problem facing the automobile industry is that conventional techniques used to lower hydrocarbons and carbon monoxide generally result in combustion conditions favoring substantial increases in NO_x.

The entire situation concerning the feasibility of the auto industry meeting the controls for 1975 and 1976 has recently been reviewed by the National Academy of Sciences Committee on Motor Vehicle Emissions (NAS, 1973). In their report to the EPA, they cite four engines that will meet the 1975 standards. These include: (1) modified, conventional internal-combustion engines with an oxidation catalyst; (2) the Wankel engine, with a thermal reactor and EGR; (3) the diesel; and (4) the carbureted stratified-charge engine.

Of these, the most favorable appear to be the stratified-charge engine and the diesel, both of which operate at substantially less penalties in fuel consumption and so on than the Wankel or the catalyst systems. Particularly impressive is the new Honda CVCC stratified-charge 2,000 cc engine. In official tests, it easily met the 1975 standards, and did so over 50,000 miles. The Honda engine is expected to become commercially available in Japan in 1974.

For 1976, much stricter NO_x controls are mandated; and other, more complex systems--including those with multi-catalyst and/or thermal reactors, or possibly fuel injection--may also be required. Here again, the Honda CVCC looks promising since it already meets the 1976 standards for NO_x (National Academy of Sciences, 1973).

NITROGENOUS MATERIALS IN THE ENVIRONMENT

Of all the gaseous nitrogenous compounds presently in the polluted troposphere, only NO_2 and PAN have been identified as being both sufficiently toxic and present at high enough levels in ambient air to be of immediate concern. Other compounds may pose real or potential health hazards (HNO_3, HNO_2, PBzN, and so on); but to date, their chemical and biological effects in polluted, ambient air are not known.

EFFECTS ON MAN

Nitrogen dioxide poses at least three major problems: (1) it is toxic to man; (2) it has a deep red-brown color, and thus in the higher levels encountered in photochemical smog it significantly reduces visibility (although it can be responsible for some beautiful, smoggy sunsets); and (3) in photochemical smog it is the precursor to ozone and PAN, both of which are highly toxic to man and plants--much more so, in fact, than NO_2 itself ("Air Quality Criteria for Photochemical Oxidants" National Air Pollution Control Administration, Publication No. AP-53, March, 1970).

Stokinger (1959), in reviewing all environmental hazards except ionizing radiation, stated:

> Airborne pollutants are potentially responsible for more of our ills than are water- and food-borne contaminants together.... Many of the conditions attributed to exposure to environmental pollutants are either accelerations of the aging process or are associated with aging. This is particularly true of the air pollutants; ozone and photochemical oxidants merely add to and hasten the oxidative destruction of the lung and other tissue sites; respiratory irritants hasten the onset of emphysema and bronchitis and would appear to promote cancer of the respiratory tract.

Both the Environmental Protection Agency and the State of California have set health-related, air-quality standards for NO_2. The EPA standard is 0.05 ppm, annual average. The California standard is 0.25 ppm per hour. There is a current debate over the federal standard. Thus, strong criticism has been voiced by General Motors scientists, who claim it is too strict in two ways: (1) the health-effects data on which the EPA based its value were inaccurate; and (2) the Jacobs Hochheiser method for measuring NO_2 in ambient air in the epidemiology study that formed a major input to the federal standard was seriously in error (Heuss, Nebel, and Colucci, 1971). The second objection has proven to be valid. The EPA is now making a major effort to obtain new air-monitoring and health data, and on that basis to reevaluate its NO_2 standard.

With the significantly increasing levels of NO_2 in urban air, the health considerations become a matter of more and more importance. One point should be noted: Although NO does not seem to constitute a health hazard in itself, it is *readily* converted to NO_2 at low ambient levels in photochemical smog and thermally at high levels of NO in exhaust plumes (as pointed out elsewhere in this paper). Thus, for example, a plume from a major fossil-fuel power plant was invisible when it left the stack; but some ten miles and more downwind from the plant, an NO_2 level of approximately 6 ppm were measured at 2,000 feet altitude. These rather startling data were taken on an air-monitoring survey utilizing an aircraft instrumented to measure air pollutants and operated by a joint NASA-Ames University of California, Riverside team (Gloria, Pitts, Behar, Reinish, and Zafonte, 1973). While there was virtually no possibility of NO_2 levels approaching that magnitude reaching the ground from that particular plume, it is sobering to observe such an efficient atmospheric conversion of nitric oxide into nitrogen dioxide.

To date there is no air-quality standard for PAN. In part, this is because PAN is presently measured at only one monitoring station in the world, the University of California Statewide Air Pollution Research Center. PAN is known to be a powerful lachrymator and to have other highly undesirable effects on man (Air Quality Criteria for Photochemical Oxidants, 1970); but such health effects have yet to be clarified and quantified in any detail.

EFFECTS ON PLANTS

Both NO_2 and PAN are phytoxicants, although the latter is far more destructive since it causes damage to certain sensitive agricultural crops and ornamental plants at levels as low as 15 to 20 ppb after four hours of exposure (Taylor and MacLean, 1970). Such plants include the petunia, tomato, dwarf meadow-grass, and romaine lettuce. An ambient level for PAN of 15 to 20 ppb is often reached, even exceeded, in areas of high photochemical smog; for example, maximums of 58 ppb at Riverside California (Taylor, 1958) and 50 ppb at Salt Lake City (Tingey and Hill, 1967).

For plant damage by NO_2 to become serious, levels on the order of 5 ppm or more generally have to be realized (Taylor, 1970). These are factors of at least five to ten more than those usually encountered in ambient air, even during heavy smog attacks. Thus, as far as plant damage is concerned, the critical role of NO_2 seems to be that of a key precursor to PAN.

It is also interesting that the alkyl analogs to PAN, peroxypropionyl nitrate PPN ($C_2H_5\overset{O}{\overset{\|}{C}}\text{-}OONO_2$) and peroxybutyrl nitrate PBN ($C_3H_7\overset{O}{\overset{\|}{C}}ONO_2$) are even more toxic than PAN itself (Taylor, 1970). Thus, although the ambient levels of these analogs are considerably lower than that of PAN, their increased toxicity would suggest they may be responsible for significant damage to field crops and ornamental plants in regions of high photochemical smog.

REFERENCES

1. E.A. Schuck and E.R. Stephens. Oxides of nitrogen, *Advan. Environ. Sci. Technol.* 1:73 (1969).

2. E.R. Stephens. The formation, reactions, and properties of peroxyacyl nitrates (PANS) in photochemical air pollution, *Advan. Environ. Sci. Technol.* 1:119 (1969).

3. A.P. Altshuller and J.J. Bufalini. *Environ. Sci. Technol.* 5:39 (1971).

4. E. Robinson and R.C. Robbins Emissions, concentrations, and fate of gaseous pollutants, *Air Pollution Control, Part II*, W. Strauss, ed., Wiley Interscience, 1 (1972).

5. H. Levy, II. Photochemistry of the troposphere. *Advan. Photochem.* 9 (1973).

6. L.A. Ripperton, A.L. Kornreich, and J.J.B. Worth. *J. Air Pollut. Cont. Assoc.* 80:9:589 (1970).

7. R. Cadle and E.R. Allen. *Science* 167:243 (1970).

8. C.E. Junge and J. Hahn, *J. Geophys. Res.* 76:8143 (1971).

9. A.L. Lazrus, B. Gandrud, and R.D. Cadle, *J. Applied Meterology* 11:389 (1972).

10. M.A. Price and E.R. Stephens. Private communication (1971).

11. K.L. Demerjian, J.A. Kerr, and J.G. Calvert. *Advan. Environ. Sci. Technol.* 4 (1973).

12. C.E. Junge. *Air Chemistry and Radioactivity*, Academic Press, New York City (1963).

13. A.P. Altshuller. *Tellus* 10:479 (1958).

14. R.L. Klimisch and K.C. Taylor. *Environ. Sci. Technol.* 7:127 (1973).

15. J.P. Lodge, Jr. and J.B. Pate. *Science* 153:408 (1966).

16. W.J. Williams, J.N. Brooks, D.G. Murcray, F.H. Murcray, P.M. Fried, and J.A. Weinman. *J. Atmos. Sci.* 29, 1376 (1972).

17. C.E. Junge, *Tellus* 8:127 (1956).

18. J.P. Lodge, Jr., A.J. MacDonald, and E. Volman. *Tellus* 12:184 (1960).

19. H.S. Johnston. *Science* 173:517 (1971).

20. M.B. McElroy and J.C. McConnell. *J. Atmos. Sci.* 28:1,095 (1971).

21. K. Schutz, C. Junge, R. Beck, and B. Albrecht. *J. Geophys. Res.* 75:2,230 (1970).

22. D.R. Bates and P.B. Hays. *Planet, Space Sci.* 15:189 (1967).

23. H.M. Foley and M.A. Ruderman. Stratospheric nitric oxide production from past nuclear explosions and its reference to projected SST pollution, Institute for Defense Analyses, Washington, D.C. Paper P-894, AD 751295 (August, 1972).

24. R. Simonaitis and J. Heicklen. *Int. J. Chem. Kinetics* 4:529 (1972).

25. J.G. Anderson and F. Kaufman. *Chem. Phys. Lett.* 16:375 (1972).

26. C. Morley and J.W.M. Smith. *JCS Faraday II* 68:1,016 (1972).

27. A.A. Westenberg and N. DeHaas. *J. Chem. Phys.* 57:5,375 (1972).

28. M.A. Price and E.R. Stephens. Private communication (1971).

29. H.S. Johnston. Project Clean Air Task Force Assessments, Vol. 4, Task Force 7, Section 3, Univ. of California (1970).

30. A.C. Stern (ed.). *Air Pollution*, Academic Press, New York City (1968).

31. K.L. Demerjian, J.A. Kerr, and J.C. Calvert. *Environ. Lett.* 3:73 (1972).

32. H. Niki, E.E. Daby, and B. Weinstock. Mechanisms of smog reactions, *In* Advances in Chemistry Series, 113 (1972).

33. J.L. Sprung, H. Akimoto, and J.N. Pitts, Jr., *J. Amer. Chem. Soc.* 93:4,358 (1971).

34. H. Akimoto, J.L. Sprung, and J.N. Pitts, Jr. *J. Amer. Chem. Soc.* 94:4,850 (1972).

35. H. Johnston and R. Graham. *J. Phys. Chem.* 77:62 (1973).

36. G.M. Hidy and S. Friedlander. Proceedings, 2nd Int. Clean Air Congress, Academic Press, New York City, (1971).

37. Air Quality Criteria for Particulate Matter. U.S. Dept. of HEW, National Air Pollution Control Administration (January, 1969).

38. H.M. Englund and W.T. Beery. Proceedings, 2nd Int. Clean Air Congress, Academic Press, New York City (1971).

39. H.R. Gloria, J.N. Pitts, Jr., J.V. Behar, R.F. Reinisch, and L. Zafonte. Airborne measurements of air pollution chemistry and transport, submitted to *J. Environ. Sci. Technol.*

40. J. Heicklen, K. Westberg, and N. Cohen. Pub. 115-69, Center for Air Environmental Studies, Univ. Park, Pa. (1969).

41. E.A. Schuck, E.R. Stephens, and M.A. Price. Paper presented at the 163rd ACS Meeting, Boston (April 9-14, 1972).

42. C.W. Spicer, A. Villa, H.A. Wiebe, and J. Heicklen. *J. Amer. Chem. Soc.* 95:13 (1973).

43. D.H. Stedman, E.D. Morris, Jr., E.E. Daby, H. Niki, and B. Weinstock. Paper, Div. of Water, Air, and Waste Chem., 160th National ACS Meeting, Chicago (September, 1970).

44. H.E. Stokinger. *Amer. Ind. Hyg. J.* 30:195 (1969).

45. B. Weinstock, E.E. Daby, and H. Niki. Discussion on a paper presented by E.R. Stephens, *In* Chemical Reactions in Urban Atmospheres, C.S. Tuesday (ed.), Elsevier, N.Y., p. 54-55 (1971).

46. K. Westberg, N. Cohen, and K.W. Wilson. *Science* 171:1,013 (1971).

47. O.C. Taylor and D.C. MacLean. *In* Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas, Informative Report No. 1, TR-7, Agricultural Committee, Air Pollution Control Assn., Pittsburgh (1970).

48. O.C. Taylor. Effects of oxidant air pollutants, *Occupational Med.* 10:53-60 (1968).

49. D.T. Tingey and A.C. Hill. The occurrence of photochemical phytotoxicants in the Salt Lake Valley, *Utah Acad. Proc.* 44:1:387-395 (1967).

50. Control Techniques for CO, NO_x and Hydrocarbon Emissions from Mobile Sources. National Air Pollution Control Admin. Pub. AP-66 (1970).

51. Control Techniques for Nitrogen Oxide Emissions from Stationary Sources. National Air Pollution Control Admin. Pub. AP-66 (March, 1970).

52. Report to the EPA. Committee on Motor Vehicle Emission, National Academy of Sciences (February, 1973).

53. Air Quality Criteria for Photochemical Oxidants. National Air Pollution Control Admin. Pub. AP-63 (March, 1970).

54. F. Stuhl and H. Niki. *J. Chem. Physics* 57:3,677 (1972).

55. J.M. Heuss, G.J. Nebel, and J.M. Colucci. *Air Pollut. Cont. Assoc. J.* 21:535 (1971).

56. D.S. Barth, J.C. Romanovsky, J.H. Knelson, A.P. Altshuller, and R.J.M. Horton. *Air Pollut. Cont. Assoc. J.* 21:544 (1971).

57. R.C. Robbins and R.D. Cadle. *J. Phys. Chem.* 62:469 (1958).

58. D.D. Davis, W.A. Payne, and L.J. Stief. *Science* 179:280 (1973).

59. P.L. Hanst. *Air Pollut. Cont. Assoc. J.* 21:269 (1971).

Crop Production

Sources of Nitrogenous Compouncs and Methods of Control

FRANK B. VIETS, JR. AND SAMUEL R. ALDRICH

THE SOURCES OF NITROGEN FOR FOOD AND MEAT PRODUCTION

A RECENT STUDY of the National Research Council--National Academy of Sciences (Alexander *et al.*, 1972) indicates that the United States needs about 18.5 million tons of available nitrogen on farms annually to produce our needs for protein and other farm-produced products. These calculations assumed an efficiency of only 3.75 percent in nitrogen use because of a low recovery by plants (estimated to be 50 per cent) and various items of waste. The nitrogen needed to produce commercial fish in farm ponds and for our substantial export of farm products was not considered.

A very high proportion of our nitrogen needs comes about because of our preferences for meat and other proteins of animal origin, such as eggs, milk, and cheese. We need about 164 pounds of nitrogen per capita each year to produce our meat and animal products, and only 10.2 pounds for the plant proteins that we consume directly. These amounts and relationships are not likely to change unless we alter our preference for proteins of animal origin. As a nation, our preference for animal proteins started to go up rapidly in the early 1940s. Population growth and change in food habits have increased our needs for available N on farms by almost 8 million tons since 1940.

Another estimate of the nitrogen needed for plant production on farms is the one made by Stanford *et al.* (1970) that all harvested crops in 1969 contained 9.5 million tons of nitrogen. Applying the same 50-percent efficiency factor for plant recovery of N used by the NAS Committee, the result is 19 million tons of available N needed on farms, close to the 18.5 million tons given in the NAS report.

The greatest speculative factor entering in these calculations of the national need for on-farm nitrogen is the assumption that the plant must

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have twice as much nitrogen available to its roots as it actually absorbs. An average recovery of 50 percent is compatible with the estimate made by Allison (1966), after an exhaustive survey of the data available. Field experiments have shown that the recovery of nitrogen by the plant can be as low as 25 and as high as 85 percent. Recovery is never 100 percent. Although an assumed recovery value of 50 percent may be satisfactory for a national average in the absence of better data, it cannot be applied to a given crop, area, or management system.

What is the source of nitrogen for crop and animal production? Several attempts have been made to make national and some state N balance sheets, but a neat tabulation of them might convey the impression that they are really more accurate than their highly speculative nature would warrant. The largest voids in information on the input side are the contributions of nonsymbiotic free-living bacteria; algae; the root-nodule bacteria of legumes; and the possibly changing inputs from the atmosphere in rain, dry fallout, and direct absorption of ammonia resulting from air pollution by various forms of fixed nitrogen. The largest void on the output side is the loss by bacterial denitrification of fixed N that shows up in all precise N-balance-sheet experiments. Little is known about denitrification in the field, except that it is favored by the low oxygen supply in the soil caused by waterlogging or by incorporating massive amounts of organic waste. Denitrification also appears to occur in oxygen-deficient microenvironments in soils that appear to be well-aerated, based on the macromeasurements usually made of oxygen in soil.

Rain and snow generally contain 0.7 to 1 ppm of N, as ammonium and nitrate. Concentrations are generally higher near urban and industrial centers than in rural areas because of the nitrogen oxides and ammonia produced by burning fossil fuels. This raises the concentration in surface runoff, which, in turn, adds enough N in most surface water to support algal growth. Runoff from forest and grassland areas may have a lower N concentration in inorganic form because of the ability of these N-starved systems to capture and store nitrogen, but the loss of inorganic N may be more than made up by the amount of organic N coming from the washout of dead plant residues and the erosion of soil organic matter.

Precipitation adds an estimated 1.5 million tons of nitrogen annually to the harvested, cropland surface of the United States (Stanford *et al.*, 1970). Alexander *et al.* (1972) estimated 6.2 million tons for the total U. S. land area. Information is very poor on whether the concentration is changing. We have few measurements on N in dry fallout, and none on the absorption of ammonia as the gas directly from the air by soils, water, and plants. Enough information is available to indicate that ammonia absorption cannot be ignored in the vicinity of some industrial plants, cattle feedlots, dairy farms, sewage-effluent lagoons, and ammonia stripping towers at tertiary sewage treatment plants.

Unquestionably in the past, the available N coming from the decomposition of soil organic matter was the largest single source of nitrogen for crop and animal production. Even now this is true in most agricultural areas--except in irrigated deserts, some highly productive sections of the Corn Belt, and many sandy coastal soils devoted to vegetable production. This is nitrogen that was stored in the soil when it was in grass and forest. The loss of soil organic N from grass and soils and from forested-area soils when they are put into cultivation has been documented extensively.

George Stanford estimated that 1.75 billion tons of organic N has been lost from the cultivated soils of the United States in the last hundred years of cultivation. How much of this N was lost by erosion, crop removal, denitrification, and the percolation of nitrate into ground water is not known. Viets and Hageman (1971) and others have suggested that deep percolation of nitrate from the decomposition of the rich prairie soils in the Midwest was a possible source of the high nitrates in the well water of many Midwest states, noted in the 1930s and 1940s and associated at that time with a high incidence of methemoglobinemia in infants. In certain areas it is likely that surface runoff or leaching from livestock feeding areas and human privies are the primary sources of high concentrations of nitrate in well water.

One current estimate of available nitrogen still coming from the exploitation of this stored N pool is 3.4 million tons annually (Alexander *et al.*, 1972). Little doubt exists in the minds of most soil scientists and agronomists that the continued exploitation of this pool of nitrogen is undesirable, since that jeopardizes the maintaining of soil physical properties and continued soil productivity. However, much needs to be learned about the specific nitrogen-supplying capacities of various soils and how these are affected by cropping, management, and fertilizer practices.

The most accurate estimate of nitrogen inputs available are those from USDA tonnage reports for commercial fertilizers. Farm and nonfarm use of commercial fertilizer N has increased from about 0.3 million ton in 1940 to over 8 million tons in 1972. Perhaps as much as 3 million tons of nitrogen were needed to offset a decrease in symbiotically fixed nitrogen. We do not have data on the legume acreage planted, but seed production of alfalfa, clovers, and lespedeza (the main N fixers) declined from 405 million pounds in 1940 to 272 million pounds in 1970.

Another interesting comparison is that the increase in fertilizer nitrogen used on farms was 6.6 million tons from 1940 and through 1968. This corresponds with the increase of 8 million tons of nitrogen needed on farms in order to produce our increased protein requirements for the same period, the latter from the NAS report.

This enormous increase in the use of fertilizer N has been part of the circumstantial evidence used by those claiming that the use of nitrogen is destroying the "balance of nature" and is causing an accumulation of nitrate in lakes and aquifers. On the basis of the cited estimates of the amount of nitrogen needed on farms, fertilizer N supplies from 30 to 40 percent of our national nitrogen needs. For corn grown under central-pivot sprinkler systems on sandy soils in parts of the West, fertilizer N must supply practically all of the nitrogen. In contrast, for wheat grown in alternate fallow-wheat systems in some parts of the Great Plains, no fertilizer N used to be needed; but the situation is changing because of higher-yielding varieties and the depletion of the organic matter in the soil.

Practically all commercial N is now the product of ammonium fixation, using air and natural gas as the raw materials. Ninety percent of the nitrogen sold to farmers is anhydrous ammonia, ammonium solutions of salts, and urea. Anhydrous and aqua ammonia make up over half of the total. From the standpoint of potential loss to the environment under most conditions of fertilizer use, the source makes little difference. Urea quickly hydrolyzes in the soil to form ammonium ions, regardless of whether that urea came from animal urine or out of a fertilizer bag. Ammonium ions, whether they come from fertilizers or the decomposition of soil organic matter, plant residues, or organic wastes, are quickly nitrified by nitrifying bacteria under favorable moisture and temperature conditions to form nitrate. Nitrate is free to move downward into the soil water.

Nitrogen transformations in nature are shown in the simplified N cycle illustrated in the figure.

Plants use mostly nitrate N because that is the form that is generally available in the soil. Most species can use ammonium, as shown by extensive work in solution and sand cultures. Yet, in the field, plants are likely to use little ammonium from fertilizers and organic sources before nitrification takes it away.

Some alternate (but expensive) "slow release" forms of nitrogen are available. These include organic wastes and manures. Urea-formaldehyde complexes have been available for more than twenty years, but are too expensive for farm use. Nitrification inhibitors such as N-serve (a pyridine compound) and potassium azide are commercially available, but are also expensive and seldom used. The side effects of using large quantities are unknown. To accomplish the slow release of N, fertilizer pellets can be encased in plastic or resinous membranes and urea pellets can be coated with sulfur. Such materials are expensive, and probably will not come into general farm use under present conditions. It is not clear whether slow-release materials would be helpful in reducing the nitrate content of surface and ground water, because, as pointed out by Allison (1965), the highest nitrogen recovery rates by crops are

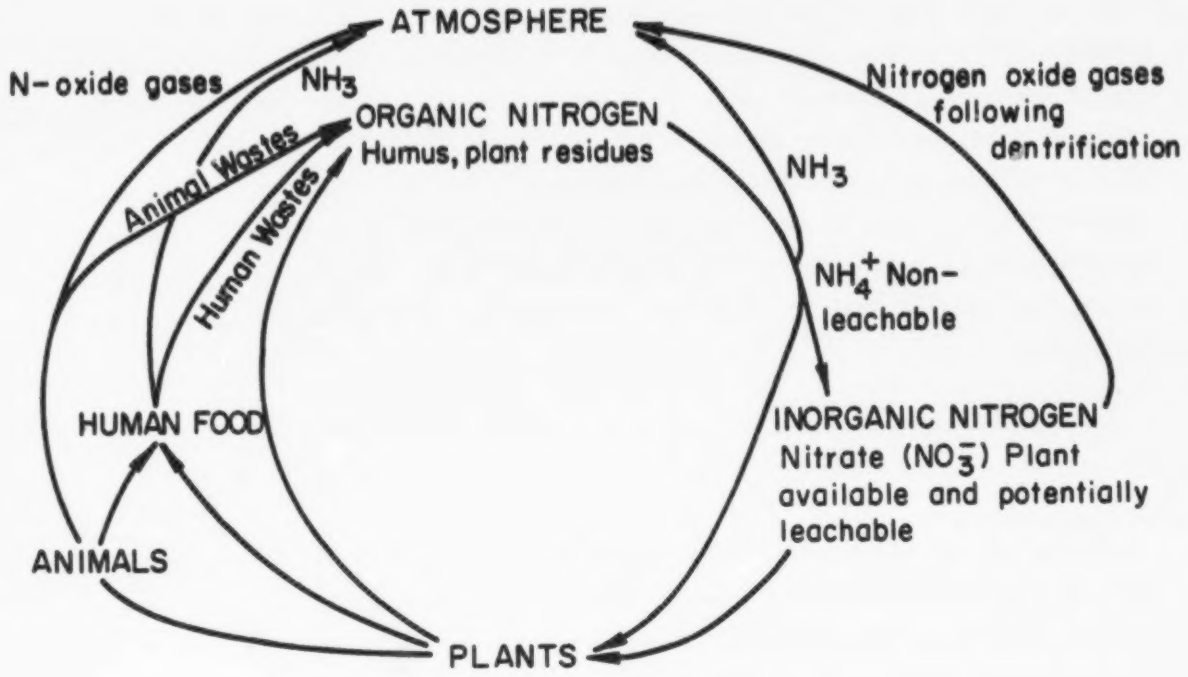
ATMOSPHERE
N-oxide gases
NH3
ORGANIC NITROGEN
Humus, plant residues
Animal Wastes
Human Wastes
Nitrogen oxide gases following dentrification
NH3
NH4+ Non-leachable
INORGANIC NITROGEN
Nitrate (NO3-) Plant available and potentially leachable
HUMAN FOOD
ANIMALS
PLANTS

FIG. 1 SIMPLIFIED NITROGEN CYCLE

observed after an application of readily available forms of nitrogen and prior to the period of rapid utilization. Delayed release may result in more nitrate after crop uptake ceases, and may also increase the possibility of leaching.

Fertilizers are a diffuse or nonpoint potential source of N pollution, except for accidental spillage in warehousing or transport. Nitrate can become concentrated in water by the evaporation of drainage in impoundments, or in the percolate from soil by the evapotranspiration of plants. In this respect, the accumulation of nitrate is similar to that of the salts associated with salinity.

Farm and ranch animals produce about 6.6 million tons of nitrogen in feces annually (Alexander, 1972). A portion of this N escapes into the air as ammonia; part is lost by denitrification. Much of this waste is deposited directly on range and farm land. Over half of the total is now produced in concentrated areas of intensive feeding operations, and the number of these direct sources of environmental contamination is growing.

The point here is the extent to which animal wastes can be substituted for commercial fertilizers. If all of this nitrogen could be saved and the loss prevented, that would amount to about 33 pounds for each of 400 million cultivated acres. Since over half of the N is deposited in diffuse sources, and probably half is volatilized by denitrification or ammonia escaping from the other half, only about 8 pounds per acre are left as a substitute for fertilizer N on crop land.

Another estimate reported by *Better Crops With Plant Food* is the one of White-Stevens that the nitrogen in the nation's total manure production totals about 2 percent of the N used in fertilizers. The manure spread on 500 million acres of arable land would amount to only 0.5 pound of N per acre.

CAUSES FOR THE INCREASING USE OF NITROGEN FERTILIZER

The use of nitrogen fertilizer has spiraled, for a number of reasons that are closely interrelated and by no means mutually exclusive.

1. The shift to proteins of animal origin. This was pointed out previously as one of the causes of our greatly increased fertilizer N needs. Increase in fertilizer N use closely parallels increased on-farmsite fertilizer N needs.
2. Soil depletion. Our once-enormous reserves of humus N--accumulated through centuries in land covered with grass or forest (N-storing systems)--have been depleted in soil fertility in many areas as a result of

soil erosion, crop removal, tile drainage, and other losses associated with cultivation. As mentioned, one estimate indicates that our crop land soils have lost 1.75 billion tons of N in the last century. Other estimates place the loss of N in rich Midwest soils at 40 percent. Long-term plot studies in the United States and Europe show that nonfertilized land decreases in productivity until it reaches a stable level that is too low for profitable farming and totally inadequate to meet the needs for food and natural fibers.

3. Better crop varieties and improved cultural practices. Continued improvements in crop varieties--through plant breeding; cultural practices; weed, insect, and disease control; irrigation; and land drainage--have led to potential yield levels at least twice those of 1940. These potential levels can be realized only if the N requirements of crops can be satisfied. Viewed another way, these higher-yielding crops will respond profitably to higher application rates for nitrogen fertilizer.

4. Declining price of N fertilizer. Since World War Two the cost of fertilizer N to the farmer has declined continuously because of advances in ammonia fixation technology, transportation (some pipelines), and bulk handling (to and on the farm). The cost per unit of nitrogen has dropped to at least half, and in some areas to a fourth of the price immediately after the war. In some areas, anhydrous ammonia has probably been sold at a loss because of an oversupply. The price has now leveled off, and will probably increase steadily because of the scarcity of natural gas.

   The declining cost of nitrogen and rising prices of other inputs and farm products has given the farmer an economic incentive to use N, and to substitute it for N-fixing legumes and for spreading manure on the fields. Farmers in semiarid and irrigated areas simply cannot afford to use soil- or reservoir-stored water for producing N-fixing legumes, unless they have a competitive cash market for hay or use those legumes in livestock programs. Although the effect of the lower prices for N on agricultural practices can be described in general terms, it cannot be separated from the other economic and technological influences that have occurred since

World War Two.

5. Less cultivated land needed. In another section, we have elaborated on the positive environmental benefits accruing during the last thirty years from the reductions in the amount of cultivated land needed to supply our domestic and foreign markets with agricultural products. The proportion of total need of the nonleguminous crops for nitrogen supplied by breakdown of soil humus may vary from almost 100 percent where no fertilizer is used to only 5 percent or less on sands with a good water supply. The gradual increase in the average yield per acre--requiring more total N--and the shrinkage in the acreage needed for cultivated crops have both contributed to a reduced role for native soil nitrogen and to a marked increase in the nitrogen deficit that must be made up with fertilizer, animal manures, and/or legumes.

6. A decline in the acreage of nitrogen-fixing leguminous crops. Alfalfa, clovers and lespedeza are capable of converting atmospheric N_2 into plant-available forms, through symbiotic nitrogen fixation in root nodules. The acreage of these crops affects nitrogen requirements in two ways. First, the need to supply nitrogen as fertilizer or from other sources is reduced when leguminous crops replace grass-forage crops which require supplemental nitrogen. Second, alfalfa, clover, and lespedeza enrich the soil in nitrogen, thus reducing the need for supplemental N for succeeding crops.

   The production of alfalfa, clover, and lespedeza seed totaled 360 million pounds in 1940 and 516 million in 1950, but declined to 244 million in 1970. Assuming that all of the seed was planted and taking into account the estimated quantities of atmospheric nitrogen fixed by these legumes, an additional 1 million tons of fertilizer N would have been needed in 1970 to replace the decline in symbiotically fixed nitrogen compared to 1940, and 3.7 million tons compared to 1950.

   The impact of large-seeded legumes that are harvested for seed (dry edible beans, field beans, and soybeans) is difficult to assess. Though capable of utilizing atmospheric N, these plants contain more nitrogen in the harvested grain than the nodules are capable of fixing. Perhaps 60 to 70 pounds per acre is a realistic expectation of the nitrogen that is fixed per average acre of field beans and soybeans. Based on the fixation of 60 pounds per acre, the change in soybean acreage (from 4.8 million in 1940 to 13.8 in 1950 and 45.8 in 1972) would have supplied 1.23 million additional tons of N in 1972 versus 1940. However, approximately 40 percent of the soybean crop is exported, reducing the N-equivalency figure to about 0.9 million ton. Theoretically, this amount is available as an offset against the 1 to 3.7 million tons of nitrogen lost to the domestic system as a result of a decline in the acreage of alfalfa, clover, and lespedeza.

SOME OVERLOOKED ENVIRONMENTAL BENEFITS FROM FERTILIZER USE

A desirable consequence of the higher yield levels obtained through the application of modern technology, including the use of fertilizers, is the substantial reduction in cropland acreage, while still meeting our national needs for farm products. Although our food needs have grown by about 1 percent a year for the last thirty years, the cultivated acres needed for this production have decreased at the net rate of some 1.4 million acres a year. To quote from the NAS study (Alexander, 1972):

> The 1968 maize crop was harvested from 55.7 million acres yielding 78.4 bushels per acre, whereas the 1940 crop came from 86.4 million acres yielding 28.4 bushels per acre. If nitrogen fertilizers were removed from the present scene, productivity would gradually decline and would eventually revert to the 1940 levels and even lower. Reserves of native soil nitrogen would be further depleted. If the productivity of American farms should return to 1940 levels, 98 million additional harvested acres of corn would be required to produce the equivalent of the 1968 crop.

The report then discusses wheat in a similar fashion. These consequences of the restriction of fertilizer use on land needs were previously pointed out by Viets (1971), Barrons (1971), and Aldrich (1972). Ibach (1966) was ahead of his time when he projected alternatives for the U. S. in 1981, pointing out that we could meet our food and natural fiber needs with a low fertility system of 8.6 million tons of fertilizer nutrients (N, P_2O_5, and K_2O) on 450.8 million acres of cropland, or a high fertility system with 26.6 million tons of nutrients on 300.5 million acres. In this case, 18 million tons of nutrients would be substituted for 150.3 million acres, or about 8.35 acres per ton of nutrients.

The environmental significance of reducing the cultivated land area is that soil erosion and pollution from farming operations are reduced and more land is available for areas of natural cover and habitats for wild life, and recreational uses. Having less land in cultivated crops permits more land to be returned to sod crops, grass, and native cover. The net result is less soil erosion. The effects of these land shifts on water pollution and erosion, and whether they were made will vary in different places. In the drier Great Plains, some former wheatland was planted to grass; in the Corn Belt, soybeans were substituted mainly for oats, wheat, and hay--increasing the erosion hazard. There are no reliable estimates about the specific effects of nitrogen and consequent land retirement on sediment-carried nutrients, although there are much experimental data on which such estimates could be based.

With less cultivated land, there is less pollution resulting from the farm operations that must be performed on land without regard to the yield level. Examples would include use of herbicides and insecticides; also, tractors that can pollute the rural air as well as the industrial area where they are manufactured. There is also a saving in the consumption of fossil fuels. Another aspect is that land is freed for natural cover, wildlife habitats, and recreational uses.

RELATION OF FERTILIZER USE TO WATER AND FOOD QUALITY

There is a dearth of data on the nitrate content of the water in streams--even more so, concerning underground waters--with which to place the nitrate problem in perspective. Common deficiencies in the records involve (1) the lack of long-term, continuous measurements to serve as benchmarks; (2) too few sampling sites; and (3) inadequate information with which to quantify the contributions from fertilizer, animal wastes, human wastes, and soil organic matter.

Nevertheless, some important generalizations can be made:

1. The nitrate concentration is increasing in some rivers that drain the great agricultural section of central U. S. The trend is erratic but undeniably upward. The increase in nitrate content is far less than is indicated in some environmental literature.

2. Selected small rivers and creeks in the Midwest sometimes exceed nitrate N level of 10 parts per million, the present standard set by the U. S. Public Health Service. Four factors are probably contributing to the excessive nitrate: the soils are inherently high in nitrogen in the form of humus; row crops, especially corn and soybeans, are the dominant ones; relatively large amounts of nitrogen fertilizer are applied; and much of the area has artificial drainage in the form of drain tiles.

   In some municipal water supplies, nitrates exceed the USPHS standard occasionally; for example, in Decatur, Illinois, and in parts of the San Joaquin and coastal valleys of California. Nightingale (1970) reported that the NO_3 in ground water was increasing as fast under the urban Fresno-Clovis area as under adjacent agricultural areas. In Illinois, the likely cause is the aggregate effect of natural conditions plus crop production practices. Urban wastes are not a significant source of nitrate in the upper Sangamon River from which Decatur obtains its water. In California, the high nitrate levels are believed to trace mainly to nitrate deposits from ancient geological periods.

3. Nitrates in many farm wells in the central U. S. range from one to ten times the standard for drinking water. This is neither a recent nor local problem. A survey of 732 wells in Iowa in 1939 revealed that 27 percent of them were above the 10 ppm limit of nitrate N, 9 percent of them were four times more than the standard, and 1 percent were ten times above it. Only insignificant amounts of nitrogen had been used prior to that time.

> Of 7,000 Illinois wells less than 25 feet deep, about 28 percent exceeded 10 ppm of nitrate N, the USPHS standard, from 1895 to 1966. In 1970, 62 per cent of the dug wells in a southern Illinois county exceeded the standard, and nearly 4 percent were ten times the standard. Minnesota experienced 139 cases of methemoglobinemia and 14 deaths, attributed to high nitrate levels in farm wells from January, 1947, to the summer of 1949--a period prior to significant use of fertilizers in that state. Early indications are that the sources of nitrates in farm wells are probably animal wastes, septic-tank fields, privies, and long-term accumulations from mineralization of humus. Fertilizer nitrogen could be an important source in shallow wells on sandy soils.

The problem of identifying the specific portion of the nitrate in a stream or in ground water that comes from the application of nitrogen fertilizer has not been solved. Kohl, Shearer, and Commoner (1971) reported their estimates of the fertilizer-N input into the Sangamon River, which feeds Lake Decatur (the Decatur, Illinois water supply). Nitrate N in the Sangamon is occasionally over 10 parts per million.

The method employed makes use of the ratio of the heavy, naturally-occurring isotope N^{15} to the more abundant isotope N^{14}. This method depends on the degree of natural enrichment of the nitrate coming from oxidation of soil organic matter with the heavy isotope and the isotope ratio in N fertilizers, which is supposed to be about the same as in the atmosphere.

theory, determining the isotope ratio of nitrate in the drainage or in the river should give an estimate of nitrate coming from current or past N fertilization. Kohl *et al.* concluded that at peak nitrate concentrations in the spring, 55 to 60 percent of the nitrate came from fertilizers. This conclusion has been challenged (Hauck *et al.*, 1972) by ten soil scientists experienced in the use of N^{15} for tracer-N studies. Various technical grounds are involved in the challenge, revolving mostly around the adequacy of the sampling. Tracer research using N^{15}/N^{14} may help pinpoint sources of nitrates, but may not prove useful unless alternative means can be found for supplying nitrogen that will produce adequate food without an equal likelihood of contributing nitrates to water.

Excessive nitrate in plants can be toxic to animals. This has been known since at least 1895, when Mayo reported the death of cattle in Kansas from drought-stricken corn. A high nitrate content in plants can produce highly toxic gases when such plants are ensiled. Deaths of infants fed canned spinach and beets high in nitrate have been reported in Europe, but not in the United States (Alexander *et al.*, 1972). Under drought conditions, some plant species accumulate nitrate in the vegetative parts and others do not. The nitrate content of seeds is never high in proportion to that of the vegetative parts of plants. Lowe and Hamilton (1967) reported 0 to 4.6 ppm in 90 samples of corn, oats, wheat, barley, and lima beans, and 8.6 to 23.8 ppm in 10 samples of soybeans. These figures contrast with 8,000 ppm in a sample of beets and 15,000 in corn stalks (also Lowe and Hamilton, 1967). Plants in the beet family can be notorious accumulators of nitrate. Plant species, drought, and shade are known to be important factors in nitrate accumulation, in combination, of course, with an adequate source of nitrogen; but nitrogen fertilizers generally play a minor role under typical growing conditions.

SERIOUSNESS OF THE NITRATE PROBLEM IN WATER, FOOD, AND FEED

In spite of the alarms spread by some environmentalists and repeated in the press, several reviewers of the problem and official groups appointed to evaluate it have, in general, judged that the present situation is not of crisis proportions, but nevertheless is one that warrants additional research and surveillance. Viets and Hageman (1971) concluded: "Our evaluation of the available information on nitrate in soil, water, foods, and feeds is that the potential for nitrate accumulation does not pose a threat of an environmental crisis. There is no indication of widespread upward trends of nitrate concentration in foods, feeds, surface or ground water." The Illinois Pollution Control Board, after extensive hearings, concluded that although an upward trend in nitrate content of some Illinois streams is apparent, there was no factual basis for restricting the application of nitrogen fertilizer. This Board recommended further study by the Illinois Institute for Environmental Quality, including the validity of the present USPHS standard for nitrate in potable water. The NAS-NRC committee (Alexander, 1972) concluded: "However, the Committee finds no evidence of danger to man, animals, or the global environment from present patterns of fertilizer use." They strongly recommended that the present upper limit of 10 ppm of nitrate-N in potable water be maintained. An expert panel convened by the Food and Agricultural Organization of the United Nations concluded in January, 1972: "It became apparent that when fertilizers are applied correctly their contribution to the nutrient content of surface waters is small in relation to nutrients derived from other sources."

Throughout the studies reported, there are words of caution, such as "recommended, proper, correct, and management," that need better definition in terms of specific crops, localities, watersheds, and basins. There are areas in which nitrate in surface and ground water is increasing. Twenty percent of our water supply comes from underground sources. The flow of surface water can usually reduce nitrate quickly, if the source of nitrate is cut off. However, underground water may have a residence time of a few months to a few centuries. Once an "old" body of water becomes polluted with nitrate, there is no way to reverse the pollution without waiting for a length of time at least equal to that during which it became polluted.

FUTURE TRENDS

What can be safely predicted for the short-term future in terms of concentration of nitrate in water as a result of crop production? We evaluate potential changes as follows.

1. The rates of application of nitrogen fertilizer per acre of corn fertilized in selected Corn Belt states are presented in Table 1. Corn receives more N than any other crop; also, it is grown on such a high proportion of land area in the Midwest that a cumulative effect is possible.

Table 1. NITROGEN FERTILIZER APPLICATION RATES ON CORN, SELECTED MIDWEST STATES, 1967-72.

	1967	1968	1969	1970	1971	1972
	Pounds per harvested acre receiving fertilizer					
Ohio	88.1	85.1	93.1	109.5	90.0	102.4
Indiana	112.2	112.3	115.3	126.2	112.6	125.7
Illinois	108.6	112.0	120.2	118.2	112.8	128.4
Iowa	89.5	104.3	108.1	106.9	100.5	110.0
Missouri	81.3	105.9	108.2	117.2	125.3	115.8
Nebraska	120.6	148.7	143.3	146.1	141.3	139.4

Sources: Cropping Practices, 1964-70, SRS-17, Statistical Reporting Service, June 1971; 1973 Fertilizer Situation, FS-3, Economic Research Service, USDA, December 1972.

The total use of nitrogen fertilizer by farm production regions is shown in Table 2. Note that the total use for 1971-72 for the 48 states shows no increase over 1970-71.

USDA data (Economic Research Service) reveal that although the total amount of nitrogen fertilizer used continues to increase, the percentage of corn fields receiving 200 or more pounds of N per acre peaked in 1969 and declined in 1970 and 1971. Some farmers were swept along beyond the optimum rates indicated by research and by unjustified, over-expectations about yields. This is of great significance because within a given set of supporting production practices, the higher the rate of nitrogen applied, the greater the proportion that remains after harvest; and hence, is at least partially leachable.

The causes for the lower application rates are probably a leveling off of the marked reduction in the cost of N (from 15 to 20 cents per pound applied to the land in the 1940s, to 5 cents in some areas by 1970) and the fact that leading farmers are bumping against a yield ceiling until breakthroughs are made in production practices. The top 5 to 10 percent of the farmers are moving ever closer to the ultimate limiting factors of natural

Table 2. CHANGE IN NITROGEN FERTILIZER USE, BY FARM PRODUCTION REGIONS

Region	Plant nutrient use, 1957-59 average	Change from 1957-59 to 1968-69	Change from preceding year 1969-70	Change from preceding year 1970-71	Change from preceding year 1971-72
	1,000 tons		*Percent*		
Northeast	152	71	4	12	-11
Lake States . .	128	337	- 6	34	- 7
Corn Belt	440	343	9	14	- 6
Northern Plains .	158	485	18	3	3
Appalachian . . .	253	81	4	9	- 8
Southeast	352	91	0	3	5
Delta States . .	229	51	7	10	17
Southern Plains .	145	436	8	0	7
Mountain	107	243	2	3	4
Pacific	342	76	7	5	10
Forty-Eight States	2,306	200	7	9	0

Source: 1973 Fertilizer Situation, FS-3, Economic Research Service USDA, December 1972.

light energy, available water in the absence of irrigation, and other climatic aspects. We may expect substantial increases in the cost of nitrogen fertilizers in the near future, as the costs of natural gas increase. Higher N costs will discourage excessive use, in the same way that lower costs may have contributed to occasional excessive use in the past.

2. The shift in crops from small grains and forage grasses and legumes to more row crops, especially soybeans, has nearly run its course. This shift is likely to have increased the nitrates in the water by accelerating the release of N from soil organic matter as a result of tillage of the soil, and by reducing the uptake of nitrates during the late fall and early spring. The proportion of row crops is now 80 to 90 percent in some areas;

hence, the potential for further increase is small.

3. The rate of release of nitrogen from soil humus is slowing down now that approximately 40 percent of the N has been used up, especially the portion more readily mineralized.
4. The peak in the rate of artificial drainage of prime agricultural land and of wet lands areas was passed long ago. Drainage increased the nitrates in surface water by speeding up the release of nitrogen from organic matter and by intercepting nitrates at two- to four-foot depths and conducting them to surface water.
5. Inasmuch as nitrate *tends* to accumulate under stress conditions, it is reasonable to expect that the nitrate concentration in leafy vegetables consumed in the U. S. is trending downward, because modern technological agriculture is designed to minimize stress in these high-value crops through irrigation, fertility balance, disease and insect control, and the like.
6. On the other side of the ledger, the nitrogen content of plant residues is increasing. Hence, they will release N more rapidly after being incorporated into the soil.

Each additional increment of N introduced into the ecosystem beyond that recovered in harvested crops is slightly more susceptible to movement into nearby water, since it is the amount of N *beyond some unknown point of balance* that determines the susceptibility to undesirable environmental effects.

We believe that in light of the available information on probable changes in cropping systems and fertilizer practices, the main increase in nitrogen in major nitrogen-using areas will be reasonably well tailored to the capacity of crops to efficiently utilize the extra nitrogen. This together with evaluation of the six points just discussed led us to predict that the concentrations of nitrates in water from agriculture will not accelerate in the near future and that the rate of change is likely to decelerate. *This suggests to us that a grace period is available, during which* *needed research on the modeling of nitrogen in the environment, the effect of alternate courses of action, and the potential danger of nitrates can be further evaluated.*

THE ALTERNATIVES

There are three fundamental objectives that interact to determine the optimum use of nitrogen fertilizer in crop production:

1. An adequate amount of high-quality food to meet human needs at an acceptable price.
2. The preservation of the productive capacity of soils for future generations.
3. A minimum undesirable effect on the environment. No strategy for food production is acceptable that fails to consider all three.

Although the focus of this paper is on the nitrate content of plants and water and on means for controlling them at tolerable levels, we are also forced to consider whether there are current problems or ones that can be expected in the future, and whether there are more desirable, viable alternatives to the present system. We shall examine these in some detail.

We shall also pose what seem to us to be hard choices for society to make in relation to the use of supplemental nitrogen in food production, and we shall raise the question of whether food production techniques should be drastically altered at this time.

Perhaps perspective on the choices available to society will be gained by stating broad, general alternatives before examining any part of the nitrate issue in detail.

1. A shift in food habits away from animal products (meat, milk, eggs) to more direct human consumption of grains. Animals do not efficiently convert the energy in graint to human food. Alexander *et al.* (1972) estimate conversion factors

for plant protein to animal protein of 4 (milk, cheese, eggs), 6 (poultry), and 9 (meat). A major shift in food habits may be possible in the long term, but we do not consider it to be a viable alternative for the short term. Alexander *et al.* noted a dramatic shift *to* livestock products in the U. S. from 1940 through 1968.

2. A reduction in food and feed exports. This would involve important humanitarian considerations as well as adverse effects on the balance of payments. Exports of farm products amounted to almost $8 billion in 1971-72, and are estimated at nearly $10 billion for 1972-73. Basically a reduction in exports would seem to ameliorate local nitrate problems by transferring them to other areas where the food deficits would of necessity be made up. Within the U. S., Illinois (a surplus grain state) could reduce production, but the grain-deficit Northeast would be forced to attempt additional production on less suitable soils, thus increasing potential nitrates and sediment-associated pollution.

3. More efficient recovery of nitrate nitrogen, irrespective of source. There are many known practices and some promising unproven techniques for increasing the efficiency of nitrate after it is added to or is formed through biological processes within the soil. Each practice by itself adds a small or modest improvement, but the aggregate effect of many practices is substantial. These will be examined in detail, but we stress at this point that high yields per acre are indispensable to efficient utilization and minimal shift of nitrates into surface and ground water.

A question to be answered is whether the upward trend in nitrate concentration of certain steams is the result of questionable strategies used in the production of food. Although it would be difficult to document with available data, it appears to us that the upward trend in either yields or total crop production is increasing at least as rapidly as the nitrate content of waters, indicating that the *nitrate load per unit of crop* produced is declining (since other sources of nitrate are increasing).

4. Removal of excessive nitrate from public drinking water and from water used in food processing. The economic and side effects on the environment of practices to control nitrate transfer into water may at some future date be greater than the cost of removing them to protect the health and the biological integrity of streams and lakes. Nitrate removal from rivers should not be ruled out.

5. Shielding susceptible individuals from consuming more nitrate than they can tolerate. The difference in tolerance between infants and older people is so great that informational programs to avoid ingestion by infants (and possibly a few genetically sensitive adults) may be preferred by society to more drastic programs designed to avoid or remove nitrate from water.

PROVEN PRACTICES FOR EFFICIENT RECOVERY OF NITROGEN ON FARMS

1. Effect of supporting practices. Since nitrogen recovery is directly related to crop yields, educating farmers about the best combination of supporting practices (date of planting; tillage; control of insects, diseases and weeds; choice of variety; harvesting to reduce field losses, and the like) is very effective in minimizing nitrate transfer into waters. Trends in crop yields during the past three decades show that educational efforts have borne fruit.

   An oft-overlooked factor in increasing yields is the continuing trend toward concentrating crops in the most suitable geographic regions. Corn acreage, for example, increased in the Corn Belt from 50 percent in 1940 to more than 80 percent by 1970.

2. Effect of application rates of nitrogen. Successive increments of nitrogen are recovered less efficiently in the harvested crop. In 18 Illinois experiments on corn, for example, four successive increments of nitrogen produced yield increases equivalent to recoveries of 79, 36, 10, and 4 percent. The lesson from this is that residual nitrogen potentially

available for leaching is concentrated near the upper end of the response curve. The economics of production are such that aiming for 95 to 98 percent rather than 100 percent of the maximum possible yield will have little effect on the farmer's profit, but may significantly reduce the potential for the leaching of nitrate. In the 18 Illinois experiments, the fourth increment of fertilizer increased grain yield 3 percent at no net profit to the farmer, but contributed 35 percent of the residual nitrogen not harvested in grain.

Producing 95 to 98 percent rather than 100 percent of the maximum possible yield would probably increase the price of the crop more than enough to maintain the aggregate gross value of the crop to farmers (Mayer and Hargrove, 1971). It would raise the cost of food a small amount and it would reduce the amount available for export to other regions or countries. Improved practices including the use of nitrogen aimed at production levels of 95 to 98 percent by less efficient farmers would have an even more important effect on food costs and on the amount of food available for export.

Planning the nitrogen rate for 95 to 98 percent of the maximum possible yield is more complicated than planning the production in a factory because of the unpredictable nature of the weather. If the yield falls substantially below expectations, there will be unusued nitrogen. If a nitrogen rate is aimed at 95 to 98 percent of the yield expected for a typical year and the weather turns out to be unusually favorable, the yield will be less than if the rate had been based on an expectation of excellent weather.

Many farmers can and do attempt to improve the likelihood of optimum nitrogen for the season by delaying part or all of their nitrogen application until after crops are planted and they can better evaluate the crop prospects.

3. Chemical form, time and place of application. Since the leaching of nitrogen is confined mainly to the nitrate form, the trend in recent years to ammonia, ammonium compounds, and urea has nearly eliminated the danger

from direct runoff or leaching of freshly applied nitrogen fertilizers.

The nearer the time that nitrogen can be applied to the time of maximum crop uptake, the less the possibility of loss. Fall application was strongly promoted in the Midwest during the 1950s and 1960s, but accounted for less than 10 percent of the total nitrogen applied in 1970. Because of greater danger of leaching, farmers have been advised against fall or early spring application on sandy soils, and the advice has been accepted. On finer-textured soils, agronomists in northern latitudes have encouraged fall application of nonleachable ammonium forms only after the soil temperature falls to the point where most of the ammonium would not convert to nitrate until the following spring. We believe that application too early is practiced on a relatively small acreage. Information programs could reduce it close to zero.

Sidedressing nitrogen after the crop is established is an accepted technique for improving the efficiency of utilization. There is, however, some risk in being unable to apply nitrogen at all if a farmer delays application until the latest possible date.

A very small amount of nitrogen fertilizer is applied to frozen, sloping fields. It is a pollution hazard locally; but since it is also uneconomic, it can be eliminated through information programs.

DIFFICULTIES OF REGULATING NITROGEN RATES

Regulations on nitrogen rates, if simple and enforceable, could not assure a goal of 95 to 98 percent of maximum yield. To attain this goal, restrictions on permissible rates would be extremely complex and would need to recognize: (1) differences among crops; (2) the susceptibility of soils to leaching and/or denitrification losses; (3) effectiveness of drainage system; (4) differences in supporting practices from farm to farm--if this evaluation were based on previous yields, the farmer would be locked into his previous system without an opportunity for improvement; (5) the yield outlook at the time of application--farmers could be held to a modest preplant application followed by a supplemental treatment at a later date, and this would involve a determination by some official and an authorization for additional nitrogen; (6) differences in the type of residues preceding the crop--amount, and the carbon:nitrogen ratio; (7) whether animal manure was applied; and (8) the possible need for adjustment in midseason due to excessive losses by heavy rains.

It is in the best interest of individual farmers to recognize all of these factors in making their decisions about the amount of nitrogen to apply.

NEEDED RESEARCH

The specific research needed in order to chart a better course in the use of nitrogen fertilizer includes:

1. The effect on nitrate content of surface and ground water of producing equivalent amounts of food using alternative sources of nitrogen--fertilizer, leguminous crops, and animal or human wastes. Eventually, the effects may also have to be confirmed on a watershed basis.
2. The influence of fertilizer rates forms and time of application on the nitrate content of surface and ground water. This will probably have to be approached on a watershed basis. Such an effort will present special cost problems because of the scale involved and the experimental design that would be required. A start has been made by the North Central Water Center (see its 1971 report).
3. Activating a network of permanent water-sampling stations in order to determine water-quality status and trends, including nitrate, to serve as permanent benchmarks. The sites should be selected so that trends within the various sources of nitrate can be separated to the extent feasible.
4. Techniques for studying the quality of ground water and identifying sources of contaminants. In some cases, the effects on the environment may be far removed in time and distance from the initial source.
5. The validity of the nitrate-nitrogen standard of 10 milligrams per liter for public drinking and food-processing water. The cost:benefit ratio of meeting the standard through alternate courses of action needs to be

determined. Part of this issue may be a comparison between major adjustments in food production in order to control the nitrate content of water versus the removal of excess nitrate from water used for drinking and food processing.

6. Techniques for reducing nitrates in the soil in late fall.
   a. Quick growing grass cover crops.
   b. Early incorporation of carbonaceous residues to tie up nitrate.
7. Understanding the factors that cause changes in the nitrogen status of soils. The variations among soils in their nitrogen-supplying capacity should be studied. Mineralizable soil nitrogen may possibly be greatly affected by future cropping, management, and fertilizer practices. Clearly, the amount of supplemental nitrogen needed will depend on the nitrogen-supplying capacities of the various soils, as well as on the crops grown. The emphasis should be on methods for evaluating residual mineral nitrogen from prior fertilization and the rapidly oxidizable nitrogen of crop residues and not on the more resistant humus nitrogen of the soil that should not be exploited further.
8. Alternating deep-rooted legumes with row crops in order to extract nitrate from soil zones below rooting depth of corn, cotton, lettuce, and the like.
9. An additional examination of nitrification inhibitors and slow-release fertilizers.
10. Some far-out techniques should be considered for the long term.
    a. Promoting denitrification *in situ*. Determine in the field the extent of denitrification in the root zone and in the aerated zone above the water table and the factors affecting rate of denitrification.
    b. Inhibit nitrification *in situ* if it is shown that crops yield equally well with ammonium NH_4^+ as the main source of nitrogen.
    c. Metering a greater portion of the nitrogen to the plant as needed in the form of foliar applications. This could be counterproductive, because the nitrogen that is not retained on leaves will be

positionally unavailable unless washed into the soil or may volatilize (NH_3) into the air.

d. Temporarily inhibit tile flow to prevent NO_3^- from reaching streams.

11. A study to determine the incentives needed in order to achieve adequate constraints on the application of nitrogen fertilizer. It is difficult to evaluate whether a combination of economic considerations, attitudes of public responsibility, the threat of restrictions on rates, together with an awareness by farmers of the results of additional technical research will provide whatever may be determined as the "needed" constraints. No assumption should be made *a priori* that such self-imposed constraints by informed farmers would be inadequate.

POLICY ON THE NITROGEN USED IN CROP PRODUCTION

The most important step in obtaining factual information on which to make proper future decisions is to fund and otherwise facilitate needed research.

Problems with excessive nitrates should be recognized as essentially local ones. Some are new. Many others are of long standing.

In the absence of reliable information about fertilizer applications and their effect on nitrates in the environment, such applications should not be regulated.

REFERENCES

Aldrich, S.R. 1972. Some effects of crop-production technology on environmental quality. *BioScience* 22:90-95.

Alexander, M., *et al.* 1972. Accumulation of nitrate. National Academy of Sciences, Washington, D.C., 106 p.

Allison, F.E. 1965. Evaluation of incoming and outgoing processes that affect soil nitrogen. *In* W.V. Bartholomew and F.E. Clark (ed.). Soil Nitrogen. *Agronomy* 10:573-606. Amer. Soc. of Agron., Madison, Wis.

Allison, F.E. 1966. The fate of nitrogen applied to soils. *Advance. Agron.* 18:219-258.

Ayers, R. S. and R. L. Branson (ed.). Nitrates in the upper Santa Anna River Basin in relation to groundwater pollution. 1973. California Agricultural Experiment Station, Bul. 861, 59 p.

Barrons, K.C. 1971. Environmental benefits of intensive crop production. *Agr. Sci. Rev.* 9:33-39.

Hauck, R.D., *et al.* 1972. Use of variation in natural nitrogen isotope abundance for environmental studies: a questionable approach. *Science* 177:453-454.

Kohl, D.H., G.B. Shearer, and B. Commoner. 1971. Fertilizer nitrogen contribution to nitrate in surface waters in a cornbelt watershed. *Science* 174: 1331-4.

Lowe, R.M. and T.L. Hamilton. 1967. Rapid method for the determination of nitrate in plant and soil extracts. *Jour. Agr. Food Chem.* 15:359-361.

Mayer, Leo V., and S.H. Hargrove. 1971. Food costs, farm incomes, and crop yields. With restrictions on fertilizer use. CAED Rpt. No. 38, Dept. Economics, Iowa State Univ., Ames, 76 p.

Stanford, G., C.B. England, and A.W. Taylor. 1970. Fertilizer use and water quality. USDA-ARS 41-168, 19 p.

Viets, F.G., Jr., and R.H. Hageman. 1971. Factors affecting the accumulation of nitrate in soil, water and plants. USDA Handbook 413, U.S. Govt. Printing Office, Washington, D.C., 63 p.

Animal Wastes

Sources of Nitrogenous Compounds and Methods of Control

JOHN C. NYE

MEAT, MILK, AND EGGS are produced by converting animal feedstuffs. The digestive process of the various types of animals results in the excretion of waste products. The nitrogenous waste of digestion comes basically from two sources. The first one is through the undigested or partially digested protein, which passes through the digestive process and leaves the body as fecal matter. Between 20 and 30 percent of the protein being fed will pass through the animal in this manner. The second source of nitrogenous waste is from the urine. Oser (1965) states that urea is "the principal end product of metabolism of protein substances in mammals." He also goes on to point out that 60 percent of the nitrogen appears in the urine as urea. With poultry, the principal product of protein metabolism is uric acid.

Briefly, the digestive process as it relates to nitrogenous compounds means that 20 to 30 percent of the nitrogen ingested by an animal in the form of proteins will pass through that animal in either undigested or partially digested proteins, found in the fecal matter; the remaining 70 to 80 percent of the nitrogen will be digested through protein metabolism, then a part of that is removed from the body in urine--primarily in the form of urea for mammals and in the form of uric acid for poultry. Both the urea and uric acid could easily be broken down into ammonia. Therefore, animal waste will contain nitrogenous compounds in the form of organic nitrogen, urea or uric acid, and ammonia.

VOLUME AND SOURCES

The following estimates of nitrogen produced in animal waste are presented in the recent National Academy of Science report, Accumulation of Nitrate:

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Animal	*Total nitrogen produced in waste*
	(million metric tons)
Dairy cattle	1.1
Beef cattle	2.9
Poultry	1.4
Swine	0.4
Sheep	0.2
TOTAL	6.0

Tables 1, 2, and 3 show the number of cattle, hogs, and chickens in various states. The 1964 Census of Agriculture showed that a majority of the livestock was still produced on relatively small-scale farms (again, see Tables 1, 2, and 3). In order to increase efficiency, there is a growing trend toward raising livestock in confinement, using large-scale livestock production facilities. This trend is most pronounced in the cattle feedlots of the southwest United States.

Wells, Meenaghan, Albin, Coleman, and Grub (1972) reported that the average number of cattle sold per feedlot per year is 100 in the Corn Belt, 1,700 in Texas, and 13,000 in Arizona. Viets (1971) pointed out that there are four primary areas where cattle feedlots are concentrated: 3 million cattle are fed in southern California and Arizona; 5 million, in the panhandles of Texas and Oklahoma; 8 million, in the central Corn Belt; and 6 million, in eastern Colorado through Nebraska and into North Dakota. He also pointed out the concentrations in the Southwest--noting that in 1968 there were 36 feedlots of over 16,000 cattle in the Southwest, while there were no feedlots of that size in the Corn Belt.

The great majority of the cattle feedlots are uncovered. As a result, they constitute the major source of pollution through the runoff after rains.

In the poultry industry, Loehr (1971) pointed out a similar trend toward intensification. He stated that, "If an egg producer does not have anywhere

Table 1. THE TEN STATES HAVING THE GREATEST NUMBER OF CATTLE AND CALVES

State	Number of Cattle[a] (1,000 head)	Average number of cattle per farm[b]
Texas	12,829	58
Iowa	7,773	59
Nebraska	6,780	91
Kansas	6,757	72
Oklahoma	5,441	53
Montana	5,238	138
California	4,775	135
South Dakota	4,543	97
Wisconsin	4,241	43
Minnesota	3,998	43
U.S.	117,916	46

[a] Crop Reporting Board, SRS, USDA, February, 1972.

[b] The Census of Agriculture, U.S. Department of Commerce. The figures are for those farms reporting cattle.

from 15 to 30 thousand birds under his control, he is not really producing a significant amount of eggs for the market." Loehr went on to note that in New York, there are farms with a million birds in confined houses. Since these houses eliminate runoff, the problem that results from large poultry operations is the proper application of manure to the soil.

In the swine industry, intensification has resulted in fewer farms producing more hogs. Muehling (1971) reported that 80 percent of the hogs sold in 1964 were produced in the ten Corn Belt states; also, that in 1966, 50 percent of the hog farms were using central farrowing houses and about 35 percent were finishing the hogs in confinement. This trend has continued. Now, very few large hog enterprises do not have an animal-waste detention facility. As a result, little of such waste is lost through runoff. The problem becomes one

Table 2. THE TEN STATES HAVING THE GREATEST NUMBER OF HOGS AND PIGS

State	Number of Hogs[a] (1,000 head)	Average number of hogs per farm[b]
Iowa	16,322	129
Illinois	7,468	110
Indiana	5,129	94
Missouri	5,120	61
Minnesota	3,692	61
Nebraska	3,691	77
Ohio	2,838	63
Kansas	2,202	51
Georgia	2,065	32
North Carolina	2,031	14
U.S.	67,540	50

[a] Crop Reporting Board, SRS, USDA, December, 1970.

[b] The 1964 Census of Agriculture, U.S. Department of Commerce. The figures are for those farms reporting hogs.

of applying the waste to the land so as to avoid the loss of nutrients.

FATE OF NITROGENOUS COMPOUNDS GENERATED BY THESE SOURCES

There are three major fates of livestock waste. It may be: (1) washed away in runoff; (2) applied to land by mechanical means; and (3) assimilated by the soil in the feedlot (a dirt lot) or lost through volatilization in the air. The runoff that can carry a sizable amount of livestock waste is the most critical problem facing the beef producer.

Table 3. THE TEN STATES HAVING THE GREATEST NUMBER OF CHICKENS FOUR MONTHS OLD AND OVER

State	Number of Chickens[a] (1,000 head)	Average number of chickens per farm[b]
California	54,893	3,200
Georgia	39,248	690
Arkansas	23,885	357
North Carolina	22,774	217
Alabama	19,377	281
Pennsylvania	18,841	592
Indiana	18,348	485
Texas	17,337	219
Florida	17,321	960
Iowa	16,629	264
U.S.	441,447	282

[a] Crop Reporting Board, SRS, USDA, April, 1972.

[b] The 1964 Census of Agriculture, U.S. Department ov Commerce. The figures are for those farms reporting chickens.

Gilbertson, McCalla, Ellis, Cross, and Woods (1970) reported that the amount of runoff depended primarily on the amount of rain, and not on the slope of the feedlot or the density of the cattle. The runoff ranged from 0 to 72 percent of the rainfall, with the total annual runoff being 40 percent of the rainfall on the unsurfaced lots. Gilbertson *et al.* reported two causes of runoff, rainfall and the melting of snow. The rainfall runoff contained a lower total nitrogen content--65 to 555 parts per million--than the winter snowmelt, which contained 1,429 to 5,763 ppm of nitrogen. In the winter runoff condition, the density of livestock did influence the amount of nitrogen, with high-density lots losing 1,056 pounds of nitrogen per acre-inch; the low-density lots, 436 pounds per acre-inch.

Miner, Fina, Funk, Lipper, and Larson (1966) reported that "more organic matter and Kjeldahl nitrogen were found in runoff (a) with low-intensity rainfall, (b) with moist conditions preceding rainfall, and (c) during warm weather." The concentration of Kjeldahl nitrogen in the runoff ranged from 94 to 1,000 mg/l from concrete lots and from 50 to 540 milligrams per liter from unsurfaced lots.

Scalf, Duffer, and Kreis (1970) studied runoff from a feedlot housing 12,000 cattle in Oklahoma and found that organic nitrogen concentrations ranged from 80 to 533 mg/l, with ammonia ranging from 60 to 208 mg/l as nitrogen. The runoff in their study ran through a 12,000-foot ditch before entering a farm pond. This ditch had no effect on the quality of the runoff, but the pond did reduce the nitrogen content by 60 to 80 percent. This reduction was caused by the sedimentation of solid matter and by dilution.

The results of these studies indicate that from "3 to 6 percent of the material deposited on a feedlot will be transported in the rainfall runoff," according to McCalla, Ellis, Gilbertson and Woods (1972). Even more is lost during winter snowmelt. When this runoff flows unchecked, it can result in major pollution, as indicated by fishkills (Scalf, *et al.*, 1970).

The improper application of manure to soils can present another source of pollution. The nitrogen content of the manure applied to the land can be lost through runoff, or it can be leached away from the root zone.

The method of applying the waste to the land can influence the quality of runoff--McCaskey, Rollins, and Little (1971). They studied the quality of runoff from grassland in Alabama where dairy waste was applied by irrigation, tank spreader, and a conventional "dry" spreader. The plots used in their study had a slope of 3.3 percent. The results of their work are summarized in Table 6. Their data seem to indicate that when less than 50 tons of animal waste is applied to the soil, there is no appreciable increase in the nitrogen lost through runoff. The method of application does not seem to affect the losses.

Table 4. TOTAL ANNUAL LOSS OF NITROGEN FROM PLOTS THAT RECEIVED DAIRY CATTLE WASTE (McCaskey, *et al.*, 1971)

Method of application	Total waste applied (Tons/A.)	Nitrogen Lost		Nitrate N (lb/A)
		Kjeldahl N (lb/A)	Ammonia N (lb/A)	
Irrigation	51.7	13.2	5.0	2.2
	51.7[a]	7.8	2.5	1.1
	34.6	6.1	5.4	1.3
	16.4	7.8	3.6	2.0
Tank spreader	32.2	4.0	1.5	1.1
	32.2[a]	5.6	2.2	3.0
	21.5	5.1	2.5	.5
	10.7	6.0	2.9	1.1
Conventional spreader	144.5	5.5	2.4	1.5
	144.5[a]	15.8	6.5	8.8
	95.8	21.3	8.6	2.7
	48.0	5.9	3.2	1.2
Control plot	0.0	5.1	1.8	1.3

[a] Plots receiving 0.5 inch of simulated rainfall weekly two days before waste application.

Another method of application that is becoming more popular is to plowdown. The injection of manure into the soil eliminates the odor problems associated with spreading. Redell, Johnson, Lyerly, and Hobgood (1971) reported results of plowing down beef manure at the rates of 300, 600, and 900 tons per acre at the Texas Agricultural Experiment Station (El Paso and Pecos). The equipment used in their work consisted of an 18-inch plow, a 27-inch trencher, a 30-inch plow, and a 50-inch disk. They reported "that the greatest opportunity for polluting surface water is by ammonia." The ammonia content in runoff from plots on which 900 tons of manure had been applied ranged from 5.04 mg/1 to 140 mg/1. The rate of application is extremely high. In work at Kansas State University--from Bernard, Denit, and Anderson (1971), 100 tons of manure from a beef feedlot was applied to a corn field. Prior to the manure application, the nitrogen content in the runoff was 15 mg/1. During the first 60 days after application, the runoff contained between 20 and 40 mg/1 of nitrogen. Again, in this study the application rate is higher than crop removal capacities.

The fate of the inorganic forms of nitrogen from land-disposed manures from dairies in the Chino-Corona Basin of California was studied by Adriano, Pratt, and Bishop (1971). They concluded that the waste of no more than three cows should be applied to an acre of pasture or cropland to insure that the NO_3 concentration would be less than 10 ppm in soil solutions below the root zone.

In summary, land application is a valid disposal technique when the manure is applied to nearly level crop land in a quantity not in excess of the crop removal capacity.

NITROGEN LOSSES

The direct losses of nitrogen from an unsurfaced beef feedlot can be sizable. Many researchers assume that 50 percent of the nitrogen in the waste will be lost prior to land application. This loss results from the infiltration of nutrients into the unsurfaced lot or the volatilization of ammonia. Gilbertson, *et al.* (1970) reported a 50- to 100-percent increase in total nitrogen in the upper two to three feet of an unsurfaced feedlot. Viets (1971) reported that "65 pounds of nitrogen per acre per year can be absorbed by a lake 1/4 mile from a large feedlot. Another lake 1 mile from the same feedlot absorbed about half as much, but that was enough to raise the nitrogen content .6 ppm. That much nitrogen was regarded as sufficient for eutrophication if other factors are favorable." He has also reported that amines that have been identified in the air of confined hog operations represent another compound which carries out sizable amounts of nitrogen.

The nitrogen lost via infiltration and volatilization has not been generally recognized as a serious problem, such as the consideration given to runoff. If a feedlot is located at a sufficient distance, at least a mile, from a major surface-water supply, ammonia losses should not cause serious problems.

AEROBIC AND ANAEROBIC TREATMENT

The new laws enacted by many states require that livestock producers store the manure and runoff for a period of time, to insure that the waste can be returned to the land in a proper manner. This trend has encouraged the development of partial waste-treatment systems. Most of these systems rely on the biological breakdown of the waste. These biological waste-treatment facilities can be categorized as anaerobic or as aerobic storage units.

The aerobic storage of livestock waste requires a higher capital investment in either mechanical aeration equipment or in the larger land areas required for lagoons. As a result of the cost of the aerobic facilities, the majority of the storage facilities for runoff and livestock waste operate under anaerobic conditions. Such anaerobic manure storage causes the livestock waste to be converted and decomposed. The nitrogenous compounds in the waste are usually converted into ammonia. Koelliker, Miner, Beer, and Hazen (1971) reported a reduction of 49 to 86 percent of the nitrogen when anerobic lagoon effluent was irrigated onto crop land. Some of the reduction was caused by the desorption of ammonia after pumping but before infiltration. This ranged from 15 to 40 percent of the total loss. Most of the reduction in nitrogen was a result of denitrification.

Under aerobic conditions, Chang, Dale, and Bell (1971) reported that between 40 and 60 percent of the nitrogen is lost during the first forty days of aeration of dairy cattle manure. Most of this nitrogen loss comes from the release of ammonia. With the loss of ammonia, there is also an increase in nitrate and nitrite after approximately the first ten days of aeration. This nitrate and nitrite buildup can go as high as 200 milligrams per liter. They also found that after nitrification, it was possible to denitrify the waste and to reduce the nitrogen content by 78 percent.

Verification of the results of Chang *et al.* (1971) for poultry waste was done by Dunn and Robinson (1972). They found a 75-percent and an 81-percent reduction in the total amount of nitrogen in an oxidation ditch after 137 days, when the dissolved oxygen fell from 4.7 to 0.4 ppm and the oxidation reduction potential fell from 375 to 10 millivolts.

These studies indicate that both anaerobic and aerobic conditions can be controlled to encourage nitrogen reductions. Other chemical and physical treatment methods such as dehydration, incineration, or pyrolysis have not received the public acceptance of the biological treatment techniques.

There are two basic approaches to the protection of the environment from nitrogenous compounds in animal waste. First, the nitrogen in the waste can be considered as a high-value product, making every attempt to utilize this in the most appropriate manner, or it can be considered as a problem, something to be removed from the waste.

There are two major ways of taking advantage of the nitrogen in the waste. First, the nitrogen can be viewed as a fertilizer for soils. This is a traditional approach, which can allow the livestock producer to reduce the amount of commercial nitrogen fertilizer he buys. The waste can be stored in a liquid form and returned to the soil by irrigating, hauling, or hauling and injecting--all in a manner that provides the greatest benefit to the crop. The manure can also be stored as a solid and returned to the soil, then utilized as a fertilizer for the crop.

The second method of taking advantage of the nitrogen in the waste is to utilize it as a source of protein for livestock feed. This can be done in a manner such as that described by Anthony (1969, 1971). He mixed the waste with grass and ensiled the product to make a feed that he calls "wastelage." Chicken manure and broiler litter have been fed to cattle by Bull and Reid (1971); also, by Fontenot, Webb, Harmon, Tucker, and Moore (1971). Flegal and Zindel (1971) studied the effect of feeding dried poultry litter to poultry.

There is some promise for refeeding some of the waste, but it is impossible to feed all of the waste to livestock without some treatment.

The waste can be fermented or aerobically converted into bacterial cells and refed to livestock as a high-protein feed material, such as that described by Holmes, Day, and Pfeffer (1971) and Nye (1971).

Holmes, *et al.* (1971) evaluated the problems of the residue from an oxidation under a confinement swine building. A continuous-flow centrifuge was used in this work. The amino acid analysis of their work showed the average product contained 1.15-percent lysine, 0.51-percent histidine and 1.15-percent arginine on a dry-weight basis.

In the work of Nye (1971), dairy cattle manure was aerobically treated in a process involving 24-hour detention and continuous culture. The biomass harvested after this treatment contained 30-percent crude protein. This product was fed to laboratory rats as half and as all of the supplemental protein. When the biomass product was fed as half of the supplemental protein, in 18 percent of the ration there was no significant effect in the rate of gain or feed efficiency of the rats.

Calvert, Morgan, and Eby (1971) suggested growing houseflies on chicken manure and feeding these houseflies to growing chickens. It is not possible for flies to utilize all of the manure.

The second way of viewing the nitrogen is as a problem, one that must be removed from the waste. With this approach, the waste is nitrified and denitrified using a technique such as described by Chang, *et al.* (1970); or Koelliker, *et al.* (1971); or Dunn, *et al.* (1972). In this technique, the waste is converted into nitrates and then, under anaerobic conditions, the nitrate is converted to nitrogen gas. This concept may be the most easily accomplished method of reducing the potential for nitrogen pollution with today's technology. Erickson, Tiedje, Ellis, and Hansen (1972) have reported on a barriered landscape water renovation (BLWR) system that could promote the denitrification of swine and dairy waste. The Kjeldahl nitrogen was reduced from 650 to 2 mg/l for swine waste, and from 300 to 3 mg/l for dairy waste. They have reported that mechanical breakdown caused the nitrate nitrogen content to jump from 10 to 200 milligrams per liter. They suggest that by 1973, it should be possible to design barriered-landscape, water-renovation systems for commercial livestock producers.

The conclusion can be drawn that at present, the most effective method of insuring against nitrogen-related pollution from livestock waste is to apply that waste to the soil, at a rate at which the crop can remove the nitrogen. Until further research can be financed and completed on the utilization and/or reduction of nitrogen, land application will be the safest way of insuring the conservation of nitrogen in animal waste.

SUGGESTIONS

Even though some form of land application is currently recommended, several systems appear to be possibilities for utilizing animal waste. The most promising technique appears to be the biological recovery of nitrogenous waste as high-protein bacterial cells. However, the most efficient method of growing of growing micro-organisms is yet to be found. An efficient harvesting process for removing the organisms from a liquid media must also be found. The complete biological protein recovery system has a broad and far-reaching effect on all organic-waste-treatment systems. Other techniques of turning animal waste into a valuable resource should also be evaluated. These processes included the recovery of fuels from the carbonaceous waste.

The reduction of nitrogen through nitrification and denitrification also needs to be examined. This biological process can be obtained in controlled aerobic liquid cultures, but the precise technique for making this a valid nitrogen-reduction process must be determined by research. The same nitrification-denitrification process occurs in soils. The influence of soil-moisture conditions, cropping practices, nitrogenous-waste application, soil acidity, and other related factors must be determined. These methods of reducing nitrogen also have application to other nitrogeneous wastes.

The nitrogen in animal wastes has long been looked on as a valuable source of plant nutrients, and has supplemented commercial fertilizers on many farms. The proper application of animal manure has prevented it from becoming a hazardous nitrogeneous waste. The increased concentration of livestock has, in some cases, eliminated the possibility of applying animal wastes to the land. Therefore, like other industries, livestock producers need these new technological advances in the utilization and/or reduction of nitrogen in order to safeguard the environment.

REFERENCES

Adriano, C.C., Pratt, D.F., and Bishop, S.E. 1971. Fate of inorganic forms of nitrogen and salt from land disposed manures from dairies, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Anthony, W.B. 1969. Cattle manure: Reuse through wastelage feeding, *Animal Waste Management*, Cornell Univer., Ithaca, N.Y.

Anthony, W.B. 1971. Cattle manure as a feed for cattle, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Bernard, H., Denit, J., and Anderson, D. 1971. Effluent discharge guidelines and animal waste technology, *Animal Waste Management*, Council of State Governments, Wash., D.C.

Bull, L.S. and Reid, J.T. 1971. Nutritive value of chicken manure for cattle, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Calvert, C.C., Morgan, N.O., and Eby, H.J. Biodegraded hen manure and adult house flies: Their nutritional value to the growing chick, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Chang, C.C., Dale, A.C., and Bell, J.M. 1971. Nitrogen transformation during aerobic digestion and denitrification of dairy cattle waste, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Dunn, G.G. and Robinson, J.B. 1972. Nitrogen losses through denitrification and other changes in continuously aerated poultry manure, *Waste Management Research*, Cornell Univ., Ithaca, N.Y.

Erikson, A.E., Agtiedje, J.N., Ellis, D.G., and Hansen, C.N. 1972. Initial observations of several medium-sized barriered landscape water renovation systems for animal waste, *Waste Management Research*, Cornell Univ., Ithaca, N.Y.

Flegal, C.J. and Zindel, H.C. 1971. Dehydrated poultry waste (DPW) as a feedstuff in poultry rations, *Livestock Waste Management and Pollution Abatement,* Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Fontenot, J.P., Webb, K.E., Harmon, B.W., Tucker, R.E., and Modre, W.E.C. 1971. Studies of processing, nutritional value and palatability of broiler litter for ruminants, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Gilbertson, C.B., McCalla, P.M., Ellis, J.R., Cross, O.E., and Woods, W.R. 1970. The effect of animal density and surface slope on characteristics of runoff, solid waste, and nitrate movement on unpaved feedlot, Univ. of Nebraska, College of Agr. and Home Economics, SB508, Lincoln.

Gilbertson, C.B., McCalla, T.M., Ellis, J.R., and Woods, W.R. 1971. Characteristics of manure accumulation removed from outdoor, unpaved beef cattle feedlots, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Holmes, L.W.J., Day, D.L., and Pfeffer, J.T. 1971. Concentration of proteinaceous solids from oxidation ditch mixed-liquor, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Koelliker, J.K., Miner, J.R., Beer, C.E., and Hazen, E.E. 1971. Treatment of livestock waste--lagoon effluent by soil filtration, *Livestock Waste Management and Pollution Abatement,* Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Loehr, R.C. 1971. Poultry waste management, *Animal Waste Management,* Council of State Governments, Wash., D.C.

McCaskey, T.A., Rollins, G.H., and Little, J.A. 1971. Water quality of runoff from grassland applied with liquid, semi-liquid, and dry dairy waste, *Livestock Waste Management and Pollution Abatement,* Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Miner, J.R., Fiena, L.R., Funk, J.W., Lipper, R.I., and Larson, G.H. 1966. Storm water runoff from cattle feedlots, *Management of Farm Animal Waste,* Amer. Soc. Agr. Eng., SP-0366, St. Joseph, Mich.

Miner, J.R. 1971. *Farm Animal Waste Management*, North-Central Reg. Pub. 206, Agr. Exp. Sta., Iowa State Univ., Ames.

Muehling, A.J. 1971. The handling and treatment of swine waste, *Animal Waste Management*, Council of State Governments, Wash., D.C.

Nye, J.C. 1971. An evaluation of a recycling waste treatment system for dairy cattle manure. Unpublished Ph.D. thesis, Purdue Univ., West Lafayette, Ind.

Oser, Bernard L. 1965. *Hawk's Physiological Chemistry*, McGraw-Hill Book Co., New York City.

Reddell, D.L., Johnson, W.H., and Lyerly, P.J. 1971. Disposal of beef manure by deep plowing, *Livestock Waste Management and Pollution Abatement*, Amer. Soc. Agr. Eng., PROC-271, St. Joseph, Mich.

Scalf, M.R., Duffer, N.R., and Kreis, R.D. 1970. Characteristics and effects of cattle feedlot runoff. Purdue Industrial Waste Conference, Purdue Univ., West Lafayette, Ind.

U.S. Dept. of Commerce, 1964 Census of Agriculture.

Viets, F.G. 1971. Cattle feedlot pollution, *Animal Waste Management*, Council of State Governments, Wash., D.C.

Wells, D.M., Meehaghan, G.F., Albin, R.C., Coleman, E.A., and Grub, W. 1972. Characteristics of waste from southwest beef cattle feedlots, *Waste Management Research*, Cornell Univ., Ithaca, N.Y.

Major Industrial Processes

Sources of Nitrogenous Compounds and Methods of Control

WILLIAM B. DAVIS

THE FEDERAL WATER POLLUTION CONTROL ACT, as amended in 1972, was passed on October 18, 1972 (Public Law 92-500). The Administrator of the Environmental Protection Agency was directed by that law to publish a list of categories of sources of pollutants which, at a minimum, include those listed in Section 306(b) (1) (A). In January of 1973, the Administrator established the following list of categories:

Pulp and paper mills
Paperboard, builders paper, and board mills
Meat products and rendering processing
Dairy products processing
Grain mills
Canned and preserved fruits and vegetable processing
Canned and preserved seafood processing
Sugar processing
Textile mills
Cement manufacturing
Feedlots
Electroplating
Organic chemicals manufacturing
Inorganic chemicals manufacturing
Plastic and synthetic materials manufacturing
Soap and detergent manufacturing
Fertilizer manufacturing
Petroleum refining
Iron and steel manufacturing
Nonferrous metals manufacturing

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Phosphate manufacturing
Steam electric power plants
Ferroalloy manufacturing
Leather tanning and finishing
Glass and asbestos manufacturing
Rubber processing
Timber products processing

With the exception of feedlots, all of the categories just listed fall under the industrial classification.

Looking briefly at the list of categories, it would seem that virtually all of the sources would be responsible for discharging nitrogen in one form or another. The magnitude and extent of nitrogen discharge, however, varies quite dramatically from one industry to the next. By contrast, the discharge of nitrogen from the manufacture of nitrate or ammonia is considerably greater than that from steam electric powerplants, which use hydrazine and amines for oxygen control in the boiler feed water.

It is not the purpose here to consider the specific unit operations and processes for each of the sources listed. In fact, a detailed review of the various categories would involve consideration of individual industries far in excess of the twenty-seven categories defined by the Administrator. A final review of this type would require coordination of information contained in the Corps of Engineers Applications filed under the 1899 Refuse Act, additional data being collected by the EPA, the various technology transfer manuals either completed or being prepared by the EPA, and various reports and textbooks on the chemical process industry (for example, *The Chemical Process Industries*, by Shreve)[1]. The intention in this paper is to give a general description of the processes that may be responsible for generating nitrogenous compounds.

LOCATION AND NATURE OF SOURCE, POINT OR DIFFUSE

Many nitrogenous compounds are created deliberately or inadvertently when atmospheric nitrogen is heated with oxygen[2]. The oxides of nitrogen are reactive. Many are absorbed in water to form the fully oxidized nitrate ion.

Most nitrogen synthesis involves the production of ammonia initially. The raw materials for ammonia production are air, water, and a carbon source (for the generation of hydrogen). Thus the location of nitrogen-fixing industries is determined more by factors such as transportation, marketing, and ultimate use than by the need to be located near to a source of raw materials. Estimates of the amount of fixed nitrogen eventually used in agriculture amount to approximately 75 percent of the total nitrogen produced[3]. Hence, most fixed nitrogen enters the environment in a diffuse manner.

The most complex nitrogen compounds are involved in industrial applications, and their discharges are often described as point sources. In many instances, the discharge from individual unit operations and processes may enter the receiving body of water from separate effluent lines. This is particularly true of old plants without facilities. Rainfall runoff from industries such as those involved in the handling of solids are generally contaminated with the product[4]. Therefore, the discharge of these industries is to some degree diffuse.

Other industries may discharge effluents into the water treated by municipal systems. In most instances, the municipal system was not designed to remove nitrogenous compounds. As a result, the industry may be discharging a point source of nitrogen indirectly through the outfall of a municipal treatment plant.

NITROGENOUS DISCHARGES FROM SPECIFIED SOURCES

Unfortunately, and with few notable exceptions, the local, state, and federal criteria for nitrogen discharges have been limited to the inorganic forms of nitrogen; and these limitations have not been strongly enforced in relation to industrial discharges. As a result, very little elimination of nitrogen from industrial discharges has resulted from the modification of in-plant procedures.

Pressures placed on industry by the Federal Water Pollution Control Act, as amended in 1972, should result in intensive efforts by industries to coordinate in-plant modifications with treatment facilities so that appreciable reductions in total discharges result (between 90 and 95 percent). A review of some preliminary EPA guidelines, however, suggests strong emphasis on reductions in Biochemical Oxygen Demand and in suspended solids. As a result, nitrogen removal would be a secondary consideration and the removal of nitrogenous compounds might be a welcomed benefit from other treatment needs, and not the result of intensive efforts to remove these compounds.

FORMS OF NITROGEN INVOLVED

INORGANIC COMPOUNDS

Nitrogenous compounds can be broadly classified as either inorganic or organic. Most inorganic forms of nitrogen are highly soluble, but may be associated with particulate matter. Inorganic nitrogen production accounts for the bulk of nitrogen-fixing manufacture. Ammonia is the most common form of fixed nitrogen produced. It is used directly as a fertilizer in agriculture or as the basis for the rest of the nitrogen chemical industry[5].

Ammonia is manufactured in a catalytic process by the reaction of nitrogen derived from the atmosphere together with hydrogen obtained by the reaction of steam, and finally with a carbon source such as natural gas. Because the catalysts involved in the reaction of hydrogen and nitrogen can be poisoned by carbon oxides, it is necessary to remove these oxides from the hydrogen stream. This procedure results in an ammonia product of rather high purity. For 1970, the U.S. Department of Commerce reported ammonia production of 13.6 million short tons in 94 establishments (Table 1). Of that 13.6 million short tons, 4.6 million were consumed in the plant of original manufacture[6].

A principal industrial use of ammonia is in the manufacture of nitric acid, which is made by the pressure ammonia oxidation process[7]. In this process, oxygen is absorbed on a catalyst and placed in reaction with ammonia to produce an imide radical, NH, which reacts with oxygen to form nitric oxide and water. The nitric oxide is further oxidized into nitrogen dioxide, which, in turn, reacts with water to form nitric acid. Traces of nitric oxide and nitrogen peroxide are contained in the tail gases from the water-absorbtion towers.

For 1970, nitric acid production in the United States was 6.7 million short tons in 72 establishments[6]. Most of this nitric acid was then converted into ammonium nitrate at the location of original manufacture. Sixty-six establishments produced 5.4 million short tons of ammonium nitrate fertilizer[6]. This fertilizer manufacture represents the principal utilization of nitric acid. Some 900 thousand short tons of ammonium nitrate were produced in 1970 for the manufacture of explosives[6]. Nitric acid is the second most-important industrial acid, and its production makes up the sixth largest chemical industry in the United States [8].

Among the inorganic nitrogen compounds, cyanide attracts immediate attention as a hazardous material. Hydrocyanic acid production was 160

Table 1. PRIMARY PRODUCTION OF NITROGEN FERTILIZER AND PHOSPHORIC ACID

Chemical and basis	Production	
	1971	1970
	Thousands of short tons	
Ammonia:		
Synthetic, anhydrous (100 percent)	13,719.3	13,569.9
Byproduct liquor (ammonia content)[a]	11.0	12.0
Ammonium nitrate (100 percent):		
Original solution[b]	6,584.3	6,475.1
Fertilizer use:		
Solution produced for sale as such for direct application	401.2	249.9
Solution produced for consumption in the manufacture of nitrogen solutions or other fertilizer materials	1,766.0	1,832.6
Solid	3,390.7	3,315.1
Other uses[c]	972.2	898.9
Ammonium sulfate:		
Synthetic (technical)	529.2	1,894.4
Byproduct, other than coke oven	1,251.8	
Byproduct (coke oven)	539.0	595.0
Nitrogen solutions, including mixtures containing urea (100 percent N):		
Solutions containing ammonia	694.0	580.4
Solutions not containing ammonia	1,211.4	1,178.5
Nitric acid (100 percent):	6,670.6	6,684.6
Urea primary solution (100 percent urea)[d]	2,820.5	3,089.0
Phosphoric acid (100 percent phosphoric oxide), total	6,034.4	5,684.6
By source:		
From phosphorus	904.9	1,040.8
Other	5,129.5	4,643.9
By use:		
For fertilizer	4,929.4	(NA)
Other	1,105.0	(NA)

REFERENCE: From Current Industrial Reports, Inorganic Fertilizer Materials and Related Acids, Summary for 1971, Series M28B(71)-13, U.S. Bureau of the Census, Wash., D.C.

(NA) Not available.

[a] Collected by or in cooperation with the Bureau of Mines.

[b] Represents the total amount of ammonium nitrate produced, including the amounts used for fertilizer, explosives, and other uses, as well as the amounts consumed in manufacturing other products, such as nitrogen solutions.

[c] Includes data for government-owned, contractor-operated plants.

[d] Collected by the U.S. Tariff Commission and published in the U.S. Tariff Commission monthly report, Synthetic Organic Chemicals, Series C. Annual data on urea produced for use in feed compounds, liquid fertilizers, solid fertilizers, and plastics are published in the U.S. Tariff Commission annual report Synthetic Organic Chemicals, U.S. Production and Sales.

thousand short tons in 1970. Of this, 110 thousand short tons were consumed in the plant of original manufacture, indicating that 50 thousand short tons of HCN are transported annually. Cyanide is widely used in the electroplating industry. However, the toxic nature of cyanide has led to increasing concern about the quantity being discharged into the environment. One result has been a shift away from electroplating processes requiring cyanide. New methods of removing cyanide are being investigated[9].

ORGANIC COMPOUNDS

Nitrogen is found in many organic compounds. A monograph on Industrial Organic Nitrogen Compounds by Melvin J. Astle[10] provides the following categories:

Aliphatic amines
Arylamines
Heterocyclic amines
Hydrazines, azo compounds, diazonium salts
Nitriles, amides, and amino acids
Isocyanates, ureas, and thioureas
Aromatic nitro and nitroso compounds
Aliphatic nitro compounds

A synoptic overview of the organic nitrogen industry in the U.S. has been provided by the U.S. Tariff Commission[11]. Nitrogen is used extensively in cyclic intermediates for the production of other substances. These are some annual production figures for these intermediates:

	Million pounds
Nitrobenzene	548
Isocyanates	513
Aniline	398

This same reference source[11] indicates that azo dyes account for 30 percent of the total U.S. dye production in 1970. The total production of azo dye was 72 million pounds in 1970, with a value of $142 million.

Cationic surface-active agents are almost exclusively compounds containing nitrogen. They include quaternary ammonium salts and primary monoamines. Total production for 1970 was 228.5 million pounds, approximately 6 percent of the total production of all surface active agents[11]. The way surface-active agents are used would indicate that these compounds enter the environment at many sources. Carboxylic acid amides are employed as nonionic surface-active agents. Production in 1970 totalled 90 million pounds[11].

Nitric acid is used in the esterification of alcohols. The most important products of such esterification are nitroglycerin and nitrocellulose. The purification of these products represents a potential discharge of nitrogen wastes; however, the nitric and sulphuric acids used in these processes are recycled[12].

Several complex organic nitrogenous compounds are used as photographic chemicals. Diazonium salts are used almost exclusively in this industry.

Urea is a nitrogen compound made by the reaction of carbon dioxide and ammonia. Production of urea in primary solution totaled 6.5 billion pounds in 1970[11]. Urea is used in feed compounds, 672 million pounds; liquid fertilizer, 2.8 billion pounds; and solid fertilizer, 2.4 billion pounds (all 1970). Industrial ureas used in the plastic industry include urea and melamine resins (746 million pounds) and polyurethane and diisocyanate resins, excluding foam and elastomers (126 million pounds)[11].

Acrylonitrile is also one of the principal organic nitrogen compounds--U.S. production, 1 billion pounds in 1970[11]. A study of the problems associated with its production illustrates the difficulties encountered by the nitrogen industry as a whole. Acrylonitrile is used in the manufacture of synthetic polymers, such as orlon and acrylon. Acrylonitrile can be produced by adding hydrogen cyanide to acetylene. It can also be produced by propylene ammino oxidation or by the propylene nitric oxide process. However, cyanide is produced as a byproduct; thus, the production of acrylonitrile represents a potential discharge of a hazardous material.

According to one study, acrylonitrile has a biochemical treatibility index of 484, rating it as the most resistant to biological treatment of the 22 organic chemicals tested[13]. Nitriles (organic cyanides) are considered only slightly toxic to humans; yet, they have a highly variable toxicity to fish. Lactonitrile (which converts to cyanide) and acrylonitrile are among the most toxic of such compounds[14]. In other uses, the polybutadiene acrylonitrile synthetic rubber production totaled 149 million pounds in 1970, while acrylonitrile butadiene styrene (ABS) and styrene acrylonitrile (SAN) thermoplastic resin production was 568 million pounds during the same year[11].

Nitrogen compounds are also involved within the chemical industry in many ways that do not appear in the final product. As an example, the soda ash industry is based on the Solvay process, which includes ammonia as a reactant. The ammonia from this process is recovered in the form of ammonium sulfate that is then recycled[15].

Ammonia is also a byproduct of other processes. The U.S. Bureau of Mines reports that the 1970 production of byproduct ammonia liquor was 12 thousand short tons (NH_3 content). The byproduct production of ammonium sulfate was 648 thousand short tons in 1969[11]. The production of both of these byproducts, however, has been declining for several years.

In addition to the thousands of nitrogen compounds that are deliberately generated as items of manufacture and commerce, it is apparent that many undefined compounds enter waste streams as undesired byproducts of chemical synthesis.

FATE OF NITROGEN COMPOUNDS

Since most fixed nitrogen is employed in agriculture as feed and fertilizer, its ultimate fate is covered in other portions of this report (as animal and municipal wastes). Much of this waste or fertilizer will eventually appear in the form of the nitrate ion in surface water. The eutrophication consequences of nitrate accumulation are generally understood[17,18]. There are biological processes for converting nitrate into atmospheric nitrogen, but the present rate of nitrate synthesis probably exceeds these natural conversion processes.

The fate of the organic nitrogen compounds is highly variable. Some, such as nylon, are biologically inert and are likely to persist indefinitely. Many compounds are slowly biodegradable; and for all practical purposes, should be considered as nonbiodegradable. These compounds are likely to be found at low levels in reveiving bodies of water, both in the overlying water and in the sediment. Because of the association of some nitrogen compounds with cancer, the full effect of these compounds on the aquatic environment and on man should be investigated[19]. Recently, the effect of chloramines on fish life has become an area of wide concern.

REDUCING THE OUTPUT OF NITROGENOUS COMPOUNDS

Because of the large number of nitrogenous compounds involved and the differing adverse environmental effects of these compounds or groups of compounds, a basic list of the most hazardous ones should be prepared. Specific guidelines for eliminating the discharge of these compounds should be developed. These guidelines would be expected to encompass the following:

Conventional treatment (biological reactors).

Conventional treatment, followed by biological denitrification.

Physical-chemical treatment.

Process modifications.

Changes in raw materials in order to reduce discharge of nitrogenous compounds.

Segregation of waste streams.

Elimination of product lines.

Intensive considerations must be given to the real hazards associated with particular nitrogenous compounds before a given solution can be recommended and enforced.

SUGGESTIONS FOR REGULATION, MONITORING, RESEARCH, AND INFORMATIONAL PROGRAMS

The regulation of compounds originating from an industry as diverse as the nitrogen industry will be difficult to achieve. Criteria and priorities must be established. The toxic effects of such chemicals should be catalogued

The most hazardous of the nitrogenous materials should be correlated with the rate of manufacture, as indicated by sources such as "Synthetic Organic Chemicals"[11] in order to pinpoint the industrial processes needing immediate attention. If the use of Synthetic Organic Chemicals is precluded by the confidential nature of the reported material, Corps of Engineer Applications filed under the 1899 Refuse Act might possibly be used.

The processes involved in the manufacture of organic nitrogen, such as the nitration reaction, generate a myriad of unclassified byproducts that are separated from the desired product and treated before discharge. Since the specific chemicals discharged from such operations are likely to be of an unknown composition, a micro and macro bioassay of the discharges from specific unit operations could prove to be valuable in determining the possible areas needing regulation immediately.

Some of the wastes are so resistant to biological degradation, that the usual criteria of water quality in terms of BOD have little meaning in determing how much of the waste materials are discharged. In addition, the presence of toxic organic materials in the waste stream is likely to inhibit bacterial processes, thus diminishing the effectiveness of biological treatment processes as well as concealing the true extent of the organic chemical content of the waste stream. In some cases, the measurable BOD increases while the stream is being treated, suggesting that hydrolysis of the waste material is taking place slowly.

In cases in which a particular waste stream is introducing a toxic material that is inhibiting the effectiveness of the total treatment process, that stream should be isolated from the process and treated independently. The identification and isolation of such streams should considerably enhance the effectiveness of the treatment operations, as well as improve the biological health of the receiving water.

In some situations, chemical reactions take place beyond the point of discharge--reactions that alter the nature of the receiving water. Ammonia has been deliberately used in combination with chlorine to produce chloramines. These chloramines have bacterial effects that last longer than those of chlorine alone. Excessive ammonia entering a water-treatment plant can increase the amount of chlorine required for effective disinfection. In some circumstances when chlorine is added to a waste stream containing the right amount of ammonia, chloramines are produced that decrease the apparent BOD and harm other organisms in the receiving water.

In high-volume manufacturing operations, such as the production of ammonia, nitric acid, and fertilizers, air and water pollution will have to be considered, in view of their particular detrimental effects on the region involved. A potential necessity for a trade-off exists in this area. Air pollution can be reduced by converting the nitrogenous products into nitrates. Yet, these represent a potential source of water pollution. Alternately, processes exist for removing nitrogen from water by means of air stripping ammonia from the water in towers at a high pH. This ammonia can represent an air-pollution problem, as well as a potential water pollution problem, since such ammonia is readily soluble in water. Thus, the total effect of any proposed treatment system must be considered fully.

Low-volume manufacturing operations, such as those involving the production of photographic chemicals and some dyes, are likely to involve relatively few points of manufacture. Many of these chemicals are likely to have only one source. If so, industry-wide standards will have little meaning. The manufacturers of such chemicals have a historical reticence concerning their methods of production and disposal. This need for secrecy and the esoteric nature of the chemicals involved indicate that effluent guidelines for such industries should be promulgated at the earliest opportunity.

REFERENCES

1. Shreve, R.N. *The Chemical Process Industries*. McGraw-Hill, New York City (1967).
2. Cornelius, W. and Agnew, W.G. (ed.). *Emissions from Continuous Combustion Systems*. Plenum Press, New York City (1972).
3. Slack, A.W. *Chemistry and Technology of Fertilizers*. Interscience, New York City (1967).
4. Bingham, E.C. "Air Pollution Problems at a Nitrogen Fertilizer Plant." In *Recent Developments in Pollution Control*: Proceedings of

the Fourth Annual North Eastern Regional Antipollution Conference Technomic, Westport, Conn. (1971).

5. Frear, G.L., and R.L. Baber. "Ammonia." Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 2, 2nd Ed. Interscience, New York City (1963).

6. "Inorganic Chemicals, 1970." Current Industrial Reports Series M28A(70)-14, U.S. Bureau of the Census, Washington, D.C. (1972).

7. Chilton, T.H. "The Manufacture of Nitric Acid by the Oxidation of Ammonia; the Du Pont Pressure Process." *Chemical Engineering Progress Monograph.* Series No. 3, Vol. 56, American Institute of Chemical Engineers, New York City (1960).

8. Powell, R. "Nitric Acid Technology--Recent Developments--1969 " *Chemical Process Review No. 30*, Noyes Development Corp., Park Ridge, N.J. (1969).

9. "Giving Cyanide the Treatment." *Chemical Week* 110(2): 55,57 (Jan. 12, 1972).

10. Astle, M.J. "Industrial Organic Nitrogen Compounds." *American Chemical Society Monograph Series.* Reinhold, New York City (1961).

11. Synthetic Organic Chemicals; U.S. Production and Sales--1970. T.C. Publication 479, U.S. Tariff Commission, Washington, D.C. (1972).

12. Miles, F.D. *Nitric Acid--Manufacture and Uses.* Oxford Univ. Press, London (1961).

13. Thompson, C.H., *et al.* "The Biochemical Treatibility Index (BTI) Concept." *Proceedings 24th Industrial Waste Conference.* Purdue Univ., West Lafayette, Ind., 413-435 (1969).

14. Henderson, C., O.H. Pickering, and A.E. Lemke. The Effect of Some Organic Cyanides (Nitriles) of Fish." *Proceedings, 15th Industrial Waste Conference.* Purdue Univ., West Lafayette, Ind. (1960).

15. Jones, H.R. *Environmental Control in the Inorganic Chemical Industry.* Noyes Data Corp., Park Ridge, N.J. (1972).

16. "Trends." *Pollution Engineering* 4(8): 31 (Nov. 1972).

17. Fruh, E.G. "The Overall Picture of Eutrophication." *Journal Water Pollution Control Federation* (39): 1,449 (Sept. 1967).

18. Yulish, J. "Are Phosphates at Fault?" *Chemical Engineering* (77): 70 (June 1, 1970).

19. Lijinsky, W. and S.S. Epstein. "Nitrosamines as Environmental Carcinogens." *Nature* 225: 21 (Jan. 1970).

Aquatic Systems

Environmental and Health Effects of Nitrogenous Compounds

RUTH PATRICK

UNDER NATURAL CONDITIONS, nitrogen enters the aquatic ecosystem by rain or by the diffusion from the atmosphere of molecular nitrogen, which is then fixed by aquatic organisms. Nitrogen may also enter by the infiltration of soil water containing various compounds of nitrogen; also, by debris, excretions, and the decomposition of terrestrial organisms that enter the aquatic system.

SOURCES OF NITROGEN IN SURFACE WATER

Man's activities constitute major sources of nitrogen. Municipal waste water may contain domestic as well as industrial waste in various proportions. According to Babbitt and Bauman (1959), such water contains the following--expressed in milligrams per liter: total nitrogen, 25 to 86; organic nitrogen, 10 to 35; free ammonia nitrogen, 15 to 50; nitrite nitrogen, 0 to 0.1; and nitrate nitrogen, 0.1 to 0.4.

Different estimates have been given for various types of storm water and combinations of storm and sewer water. Woodward (1961) reported that constituents of storm water runoff from a 27-acre, residential-like commercial area with separate storm and sanitary sewers were for the storm water: total nitrogen, 3.1 mg/l; and inorganic nitrogen, 1 mg/l. Sylvester (1959) gave mean values of 2.01 mg/l for total Kjeldahl nitrogen and 0.53 mg/l for N as NO_3 for runoff from urban streets.

The runoff from fertilized fields also contributes nitrogen to the aquatic environment. Allison (1955) estimated that erosion and leaching together account for about 65 percent of the losses of nitrogen from fertilizer applied to the soil. Weibel, *et al.* (1966) stated that there were 7.8 mg/l of total nitrogen and 4.1 mg/l of inorganic nitrogen in the runoff from a 1.45-acre cultivated field of winter wheat in Ohio from March, 1964, to February, 1965.

Livestock wastes are becoming a greater problem because of the increasing number of concentrated, centralized feedlots. In animal feedlots, drainage ammonia is a major nitrogen constituent caused by the hydrolysis of urea. According to Pomeroy and Orlob (1967), typical concentrations of ammonia may run as high as 150 mg/l of nitrogen as NH_3. High nitrate concentrations in ground water have been traced to contamination from feedlots and livestock wastes in Missouri, Minnesota, and other areas.

The deforestation of a watershed may also have a tremendous effect on the amount of nitrogen entering a stream. Likens, Bormann, and Johnson carried out some experiments on Hubbard Brook. They found that in the area which had been deforested, the nitrate concentration changed from 0.9 mg/l before the vegetation was removed to 53 mg/l afterward. This increase in nitrate mobilization seemed to be caused by an increase in microbial nitrification. The result of this increase in the amount of nitrates entering the stream produced unusual algal blooms (personal communication) that were not present before deforestation took place (Likens, Bormann, and Johnson, 1969).

In the natural world, there is a balance between the (1) input of nitrogen and (2) that which is utilized by the aquatic biosphere, deposited in sediments, and returned to the atmosphere. The cycling of nitrogen in the biosphere is relatively complex. Molecular nitrogen must be oxidized in the form of ammonium or organic compounds so it can be utilized by organisms. Molecular nitrogen may be oxidized by lightning in the atmosphere, or it may be reduced to form ammonia by various bacteria (azobacteria) and blue-green algae. That second process requires energy which is derived from the utilization of pyruvic acid (Fogg, 1956, and Burris, 1969).

A list of the blue-green algae known or believed to be able to carry out this process is given in Table 1. Ammonia in the aquatic environment may

Table 1. CAPABILITIES OF VARIOUS BLUE-GREEN ALGAE FOR N_2 FIXATION

	Certain	Doubtful	Nil
Anabaena flos-aquae		x	
A. circinalsis		x	
A. scheremetievii		x	
Anabaenopsis circinalis	x		
Anabaena spirooides	x		
Anabaeneesis spec.	x		
Aphanizemenon flos-aquae			x
Gloetrichia echinulata	x		
Microcystis aeruginosa			x
Oscillatoria rubescens			x

be taken in by nitrosomas bacteria and changed to nitrites which, in turn, are taken up by nitrobacteria and changed into NO_3 nitrogen. Some anerobic bacteria such as the *Pseudomones* group utilize NO_3 as an oxygen donor and reduce it to N in the process (Martin and Goff, 1972).

Most algae, bacteria, fungi, and other aquatic plants absorb nitrates, ammonia, or various amino acids from the aquatic environment. A few can utilize molecular nitrogen (Table 2). Within the cell, however, ammonium is used in the formation of amino acids. Whether or not a plant uses ammonia or nitrates as a nitrogen source depends on the plant species involved and also on the pH of the medium. For example, *Scenedesmus quadrata*, a green alga, will utilize NH_4 or NO_3 within a pH range of 7 to 9; but above 9.5, no growth occurred with NH_4, although some growth took place with NO_3 up to a pH of 11 (Hutchinson, 1957).

Nitrate nitrogen is the preferred form of nitrogen for *Botryoccoccus Braunii* and for some diatoms (Chu, 1942). *Chlorella* can utilize ammonium, nitrite, nitrate, acetamine, and other amino acids (Hutchinson,

Table 2. **ABSORPTION CAPABILITY OF VARIOUS AQUATIC PLANTS**

	Organic N	N(NH_3)	N(NO_3)	N_2
Some bacteria and Eumycetes, some species of Euglena	x			
Some bacteria and Eumycetes	x	x		
Most bacteria, Eumycetes, algae, and higher plants	x	x	x	
Some bacteria and blue-green algae. .	x	x	x	x

1957). Hutchinson (1967) reported that the flagellates *Euglena* and *Phacus* prefer ammonia as their nitrogen source.

As stated by North, *et al.* (1971), low concentrations of amino acid in water near the shore (about 1 micromohl per liter) can support the nitrogen requirements of *Chalmydomonas*. Macroscopic algae may also utilize amino acids. *Ulva* and *Enteromorpha* show rapid accumulations of amino acids in dilute solutions. Other algae which have been shown to utilize amino acids are the diatoms *Skelatonema costatum, Cyclotella nana, Melosira* sp., *Nitzschia closterium, N. ovalis,* and *Thalassiosira fluviatilis,* and other green algae such as *Chlorella* sp., *Chaetomorpha, Codium, Enteromorpha,* and *Ulva*. The brown algae are *Colpomenia, Egrethia, Hesperophycus, Macrocystis, Pachydictyon, Pleetia*; and the red algae are *Bossiella, Corallina, Endocladia, Gelidium, Gigartinea, Gracilariopsis, Lithothrix, Porphyra,* and *Weeksia*.

The kind of nitrogen compound as well as the amount of nitrogen an aquatic plant will absorb depend on the conditions of the plant and the concentration in the medium. As pointed out by Fitzgerald (1968), the condition of the plant--that is, whether or not it is nitrogen-starved--greatly influences the uptake. Table 3 sets forth the differences in uptake rates for various algae and other aquatic plants.

Table 3. UPTAKE RATES: ug/l NH_4-N ABSORBED/10 mg DRY WT/HR BY ALGAE

Algae	Complete medium	N-limited medium
GREEN ALGAE		
Chlamydomonas chlamydoeama . . .	0	18
Scenedesmus dimorpha	17	62
Cladophora sp.	3	18
Spiroqyra sp.	7	30
DIATOMS		
Nitzschia sp.	2	13
BLUE-GREEN ALGAE		
Microcystis aeruqinosa	16	36
Anabaena flos-aquae	0	1
Aphanizomenon flos-aquae	3	0
SPERMATOPHYTES		
Lemna minor (duckweed)	4	18
Ceratophyllum	10	7

Modified from Fitzgerald (1968).

These studies show that a plant starved for nitrogen will have a much greater nitrogen uptake rate than one in a medium with sufficient nitrogen. Furthermore, the amount of nitrogen that is accumulated within the plant will vary according to the concentration of nitrogen in the medium.

For example, in the common aquarium plant, *Elodea*, the increase in nitrogen in the tissue will be linear with the increase in dry weight until the nitrogen reaches 1.3 percent of the dry weight. Concentrations of nitrogen in the tissues may increase beyond this amount, but the increase in cells will not be linear. In fact, it may be very little. Gerloff (1969) has referred to this as "luxury consumption," because it is an accumulation of nitrogen beyond that necessary for growth. This phenomenon is often found in polluted waters where nitrogen compounds are excessive.

Aquatic plants, like terrestrial plants, utilize many chemicals for food, growth, and reproduction. Under optimum conditions, those chemicals are in the correct amounts and ratios for a given species. A shift in amounts and ratios will bring about a change in the kinds of species or in the abundance of a species. This often means a shift from species with high predator pressure to those with the opposite. The result is a large standing crop, with the accompanying effects of nuisance growths. Thus, imbalances in nutrients without increases in concentration may develop nuisance problems.

In natural lakes and streams, the ratio of nitrogen to phosphorus varies greatly. Part of this variation is due to the chemical and physical conditions of the body of water being studied, but it also depends on whether one is talking about total nitrogen and phosphorus or soluble nitrogen and phosphorus. For example, Hutchinson (1957) discusses the phosphorus and nitrogen in Wisconsin lakes. The average N as ammonia is 307 milligrams per cubic meter. The average N as NO_3 is 64 milligrams per cubic meter, with a total of 371 milligrams per cubic meter of soluble nitrogen. The mean amount of soluble phosphorus for lakes in northern Wisconsin is 3 milligrams per cubic meter, or an approximate ratio of 127 to 1. However, if one considers the total phosphorus (45 mg per cubic meter), then the ratio of total phosphorus to soluble N is roughly 8 to 1.

Although these ratios are variable, one often finds ranges of N to P from 50:1 to 1:1, depending on the degree of eutrophication of the lake. However, in lakes in which phosphorus appears to be limiting, such as Hutchinson (1967) found on occasions for Linsley Pond, the ratio of inorganic combined N to P was 0 to 220;1. The amounts of nitrogen and phosphorus characteristic of lakes with various levels of eutrophication are given in Table 4, as set forth by Vollenweider (1968). Sawyer (1947) working on lakes in Wisconsin presented the hypothesis that an aquatic bloom would develop if the inorganic N is greater than 300 milligrams per cubic meter and if the phosphorus is greater than 10 mg/m^3 in a lake at the beginning of the growth period for algae and other plants. Vollenweider (1968) stated that findings in Europe support this hypothesis.

Table 4. INORGANIC N CONCENTRATIONS IN LAKE WATER ASSOCIATED WITH DIFFERENT TROPHIC LEVELS

Increasing levels of nutrient availability	Inorganic N *mg/l*
Ultra-oligotrophic	0.2
Oligo-mesotrophic	0.2 to 0.4
Meso-eutrophic	0.3 to 0.65
Eu-polytrophic	0.5 to 1
Polytrophic	1.5

Source: Vollenweider (1968)

In flowing water, the concentration of nitrogen may be somewhat greater without producing excessive growths. In White Clay Creek in Eastern Pennsylvania (Chester County), we have found that the nitrogen concentration may vary from 1 and 2.5 mg/l without producing excessive algal growths. The nitrogen is mainly in the form of nitrates, and the amounts of ammonia or nitrites present are very low. Vollenweider (1968) reported that similar concentrations are characteristic of streams in Europe, ones that do not sustain nuisance growths.

The reason rivers can tolerate higher levels of nitrogen, phosphate, and other nutrient concentrations versus lakes is probably the result of differences in the cycling of nutrients. Nutrients that enter a lake are usually taken up by the growth of phytoplankton and zooplankton organisms, as well as by benthic species. Upon the death of these organisms or by excretions from them, the nutrients become absorbed onto sediments and settle-out in the bottom of the lake.

During the summer, particularly in deep lakes, a stratified anaerobic zone may develop. This brings into solution the nutrients that formerly were precipitated out of solution. During the fall overturn, these nutrients are recycled and again reach the epilimnion, where they are converted into plant and animal organisms. This continual recycling of nutrients brings about a buildup in concentrations within the lake over time. The only nutrients that leave the lake are those in the outfall of water and sediments from the lake and those that leave the lake in the form of emergent organisms. The lake or pond functions as a sink for the accumulation of nutrients.

By contrast, the river is a flowing system. Nutrients are always entering and leaving any given section. They only accumulate temporarily in the sediment of slack water and in pools, from which they are usually flushed out by floods occurring sporadically throughout the year. Because the sediments in the bed of a stream or river are typically in an oxidized state, they do not produce soluble nitrogen compounds. It is only in deep pools that anaerobic respiration may take place, thus yielding redissolved nutrients. It is this continual flushing of nutrients that enables the flowing-water ecosystem to tolerate higher nitrogen levels without producing nuisance growths.

In estuaries and in the open sea, nitrogen compounds--particularly ammonia and nitrates--are often present in very low concentrations; and as a result, limit the total biomass and determine the types of species it contains. For example, Sverdrup and Allen (1939) and Sargent and Walker (1948) related diatom populations to the large-scale eddies and areas of upwelling water off the coast. These upwelling waters from the deep sea are rich in nutrients, particularly nitrogen.

Much of the year, the surface water off southern California is depleted of its plant nutrients, especially nitrogen. Nitrates are undectable at the surface, and ammonia concentrations are less than one micromohl. Thus, any increase in nitrogen usually results in a greater algal bloom. Enriched waters in the open sea usually bring about diatom blooms; whereas an increase in nitrogen along the shore often brings about blooms of dinoflagellates, which are referred to as "red tides."

This difference in the type of bloom is probably partly due to the differences in the form of nitrogen in the two areas. In southern California, nitrate is the major form of nitrogen associated with upwelling. Ammonia is the principal form of nitrogen found in sewage discharged along the coast. Phytoplankton appear to utilize both forms of nitrogen equally well--although the composition of plankton, especially the C-N ratios, may vary somewhat with the nitrogen source used for growth (Eppley *et al.*, 1971).

TOXICITY OF NITROGEN COMPOUNDS TO AQUATIC LIFE

There are two natural forms of nitrogen that are most toxic to aquatic life. These are nitrogen as a gas dissolved in water and ammonia. The toxic effect of molecular nitrogen in water occurs when there is a sudden rise in the temperature of a body of water in which fish are confined. This may happen below the dam in a river, a place where fish congregate in the cold water in the pools. If the flow of water is curtailed for any reason, the water in the pool can warm up very rapidly, particularly in the summer. This increase in temperature allows gas bubbles to be released in the blood of fish and embolism occurs. This is a disease similar to "the bends" in humans. Fish kills caused by embolism have been reported below the dam on the Susquehanna in Pennsylvania and below the dam in the Roanoke River in Virginia.

The toxicity of ammonia is related to the pH, since only the un-ionized molecule is toxic. The toxicity may increase rapidly with slight increase in the pH level (Burrows, 1964). Greater concentrations of dissolved oxygen and carbon dioxide, elevated temperatures, and bicarbonate alkalinity are also important in increasing ammonia toxicity (Lloyd, 1961). Various effects of ammonia toxicity have been reported. Burrows (1964) described major gill damage to juvenile salmon when the un-ionized ammonia concentrations were as low as 0.01 milligrams per liter. Data given by Lloyd and Herbert (1960), Ball (1967), and Lloyd and Orr (1969) indicate toxicities below 1 mg/l for fish.

Little is known about the toxicity of nitrites in relation to aquatic life. Considering its toxicity to warm-blooded invertebrates, this compound deserves further study. Recent investigations by R. Krauss indicate that N and NO_2 are lost from the cultures of *Chlorella sorokiniana* growth in nitrate and in urea.

Many other nitrogen compounds have been shown to be toxic to aquatic life. Some of these are acrylonitrils, nitroamylene, nitrobenzene, nitrophenol, chloroamines, diethylamine, dinitrocresol, dynitrophenol, ethylamine, ethylenediamine, triethylenediamine, and trinitrophenol.

CONCLUSIONS

Although nitrogen is an essential nutrient chemical for all living organisms, it is now occurring in concentrations in our waterways that are hazardous to many forms of aquatic life. These concentrations are helping to bring about increases in the abundance of species that cause nuisance growths. Some of these, such as certain species of blue-greens, produce substances that are toxic to many forms of aquatic life as well as to terrestrial organisms. The concentrations of nitrates in some ground and surface water are high enough to be dangerous to man. For these reasons, efforts should be made to maintain the levels of N as NO_3 or NH_4 at the beginning of the growing season to less than 0.3 mg/l in lakes and not more than 1 mg/l in free-flowing waters. In some instances, such requirements may be too strict because one cannot universally establish a concentration of N that will prevent algal blooms in all kinds of water. Therefore, it may be necessary to run a laboratory test such as the Provisional Algal Assay Procedure (1969) to determine what additions of N will produce algal blooms in the type of water in question. Since un-ionized ammonia is toxic to many forms of aquatic life, its concentration should be controlled so it does not exceed 0.02 milligrams per liter. Care should also be taken not to change to any great degree the existing N:P ratio. In water used for drinking, the level of nitrogen as $N\text{-}NO_3$ should be less than 10 milligrams per liter.

LITERATURE CITED

Allison, H.E. 1955. The enigma of soil nitrogen balance sheets. *Advances in Agronomy*, 7:212-250.

Babbit, H.E. and Bauman. 1958. *Sewerage and sewage treatment*. John Wiley and Sons.

Ball, T.R. 1967. The relative susceptibilities of some species of freshwater fish to poisons. I. Ammonia. *Water Research*, 1:767-775.

Burris, R.H. 1969. Progress in the biochemistry of nitrogen fixation. Proceedings of the Royal Society of London, ser. B, Botany, 172:339-354.

Burrows, R.E. 1964. Effects of accumulated excretory products on hatchery-reared salmonids. U.S. Bureau of Sport Fisheries and Wildlife Research Report No. 66, p. 12.

Chu, S.P. 1942. The influence of the mineral composition of the medium on the growth of planktonic algae. I. Methods and culture media. *Journal of Ecology*, 30:284-325.

Eppley, R.W. *et al.*, 1971. Phytoplankton growth and composition in shipboard cultures supplied with nitrogen, ammonia, or urea as the nitrogen source. *Limnology and Oceanography*, 16(5):741-751.

Fitzgerald, G.P. 1968. Detection of limiting or surplus nitrogen in algae and aquatic weeds. *Journal of Physiology*, 4(2):121-120.

Fogg, G.E. 1956. Nitrogen fixation in photosynthetic organisms. *Annual Review of Plant Physiology*, 7:51-70.

Gerloff, G.C. 1969. Evaluating nutrient supplies for the growth of aquatic plants in natural waters. *In*: Eutrophication: causes, consequences, correctives. National Academy of Sciences: 537-555.

Hutchinson, G.E. 1957. A Treatise on Limnology. *Geography, Physics and Chemistry, Volume I*. John Wiley & Sons: 1,015 p.

Hutchinson, G.E. 1967. A Treatise on Limnology. *Introduction to Lake Biology and the Limnoplankton, Volume II*. John Wiley and Sons: 1,115 p.

Joint Industry/Government Task Force on Eutrophication--Provisional Algal Assay Procedure. 1969. P. O. Box 3011, Grand Central Station, New York City.

Likens, G.F., F.H. Bormann, and N.M. Johnson. 1969. Nitrification: Importance to nutrient losses from a cutover forested ecosystem. *Science*, 163(3,872):1,205-1,206.

Lloyd, R. 1961. Effect of dissolved oxygen concentration on the toxicity of several poisons to rainbow trout. *Journal of Experimental Biology*, 38:447-455.

Lloyd, R. and D.W.M. Herbert. 1960. The influence of carbon dioxide on the toxicity of un-ionized ammonia to rainbow trout. *Annals of Applied Biology*, 48:399-404.

Lloyd, R. and L.D. Orr. 1969. The diuretic response by rainbow trout to sub-lethal concentrations of ammonia. *Water Research*, 3:335-344.

Martin, D.M. and D.R. Goff. 1972. The role of nitrogen in the aquatic environment. Academy of Natural Sciences of Philadelphia, Contributions from the Department of Limnology, No. 2. 46 p.

North, Wheeler J. *et al.* 1971. Marine algae and their relations to pollution problems. Keck Engineering Laboratories, California Institute of Technology. 14 p. plus charts.

Pomeroy, R.D. and G.T. Orlob. 1967. Problems of setting standards and of surveillance for water quality control. California State Water Quality Control Board, Publication No. 36. 23 p.

Sargent, M. and T.J. Walker. 1948. Diatom populations associated with eddies off southern California in 1941. *Journal of Marine Research*, 7(3):490-505.

Sawyer, C.N. 1947. Fertilization of lakes by agricultural and urban drainage. *Journal of the New England Water Works Association*, 61: 109-127.

Sverdrup, H.U. and W.E. Allen. 1939. Distribution of diatoms in relation to the character of water masses and currents off southern California in 1938. *Journal of Marine Research*, 2:131-144.

Sylvester, R.O. 1959. Nutrient content of drainage water from forested urban and agricultural areas. Algae and Metropolitan Wastes, U.S. Public Health Service Document No. 16524.

Vollenweider, R.A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters with particular reference to nitrogen and phosphorus as factors in eutrophication. Organization for Economic Co-operation and Development, Paris. DAS-CSI-68.27.

Weibel, S.R., R.B. Weidner, J.M. Cohen, and A.G. Christianson. 1966. Pesticides and other contaminants in rainfall and runoff. *Journal of the American Water works Association*, 58:1,075-1,084.

Woodward, L. April, 1961. Ground water contamination in Minneapolis and St. Paul suburbs. *In*: proceedings of a 1961 Symposium on Ground Water Contamination. Robert A. Taft Engineering Center, Technical Report W61-5.

Environmental and Health Effects of Nitrogenous Compounds

JOSEPH SIMON

THE IMPORTANCE OF NITROGENOUS COMPOUNDS in animal health and/or disease is unknown, because of the limited nature of clinical and field observations, clinical pathologic and necropsy reports, and experimental studies.

Historically, the studies of outbreaks of cornstalk poisoning[58] in Kansas and oat hay poisoning[12,3,8] in the High Plains States incriminated nitrite, obtained from nitrate reduction, as the intoxicant.

Nitrite intoxication is usually categorized as acute and lethal, or as chronic and sublethal. A diagnosis of acute nitrite intoxication can usually be made. Diagnosing sublethal or chronic intoxication is difficult. In all probability, chronic nitrite poisoning has been an "ash can" diagnosis for diseases of unknown etiology.

Because of a complex digestive system that permits the reduction of nitrate into nitrite, herbivora, cattle[54,66,85,89] and horses[4] are affected most frequently by nitrite intoxication. An occasional report suggests that intoxication may be encountered in other species[28,3].

NITROGENOUS COMPOUNDS INVOLVED

Although the literature contains reports of nitrate intoxication, nitrate is essentially innocuous. It is its reduction into nitrite that provides the hazard of intoxication[62,98]. In addition to nitrite, these other nitrogenous compounds have been incriminated in animal disease: urea, ammonia, oxides of nitrogen, hydroxylamine, and nitrosamines.

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TYPES OF HAZARD

ACUTE OR LETHAL NITRATE (NITRITE) TOXICITY

Acute nitrite toxicity in animals is characterized by hypoxia, the result of methemoglobin[53,69,82] formation. Usually, the transformation of 70 percent of hemoglobin into methemoglobin is believed to result in death. Basically, nitrite oxidizes iron from the ferrous to the ferric state, depriving hemoglobin of its ability to transport oxygen.

Experimental studies have shown that in animals fed either nitrate or nitrite, the production of methemoglobinemia[78] is contingent on numerous factors--such as the species[14,98]; microbial flora[54,66,85,89]; ions[85]; Mo, Cu; sex[81]; pH[85]; diet[47]; vitamin C levels[45]; age[6,52]; pregnancy[59,61]; disease state, concomitant infections[85]; and/or neoplasia.

Nitrite may react with hemoglobin and methemoglobin in the formation of a reversible complex between excessive free nitrite and ferric heme groups of methemoglobin[79]. An analytic problem could result, because this complex in nitrited erythrocytes may result in lower methemoglobin values in spectrophotometry.

It has been shown *in vitro*[68] that the addition of nitrite to blood may result in a compound, nitrosohemoglobin. The amount formed varies with the animal species and is greatest in actively metabolizing red blood cells. *In vivo*, in sublethal nitrite intoxication, and under certain conditions in which nitrite methemoglobin is not formed, nitrosohemoglobin forms with conversion to nitrosomethemoglobin, which decomposes into methemoglobin and nitrous oxide. The relative importance of this alternate means of methemoglobin formation is unknown. The age, health status, and the species involved constitute important variables. Experimental studies are needed for clarification.

Nitrites and organic nitrates are known vasodilators in monogastric animals[38,67]. In cattle, limited work[2] suggests that in this respect they probably are of little importance.

CHRONIC OR SUBLETHAL NITRATE (NITRITE) TOXICITY

Experimental evidence suggests that nitrate and/or nitrite ingestion may interfere with thyroxine synthesis[7,99] in rats and sheep. The effect is transitory[8,9,11,91,92]. Under optimum conditions, ruminant animals do not develop thyroxine deficiency when fed low levels of nitrate. In cases of iodine deficiency or the ingestion of other goiterogenic substances, however, nitrate may augment relative decreases in thyroid secretion[30].

There is considerable confusion about the effect of nitrate (nitrite) in vitamin A metabolism[15,16,27,34,39,40,43,46,72,86,98]. Apparently, the formation of nitrite from nitrate requires an almost neutral pH, which occurs in the rumen. Following formation, the nitrite is reduced or absorbed so that little will be found in the true ruminant stomach, the abomasum. Nitrite destroys carotene and/or vitamin A at a pH of 4. Hence, in the normal runinant, nitrite probably is of little significance in carotene and/or vitamin A metabolism[16,20,2],32,42,64,80].

In some cases, in which carotene or vitamin A losses have occurred in the processing of feed prior to ruminant ingestion, nitrates or nitrites have been blamed for avitaminosis A[25]. Field reports have been made during the winter months in Illinois of feeder steers fed yellow corn grown on highly fertilized fields manifesting joint and pectoral edema, signs reported to be associated with vitamin A deficiency. The administration of high dosages of vitamin A has been reported to result in a cure; admittedly, these comments are empiric]100].

In monogastric animals[17,40,98], the acid pH of the stomach in association with ingested nitrite may affect carotene and/or vitamin A metabolism. In swine with reduced liver stores of vitamin A, the ingestion of water containing 0.08 percent nitrite (240 ppm -- NO_2-N) has been associated with reduced weight gain and reduced food intake[96].

Nitrates (nitrites) in rations or water[96] have been incriminated--in some cases with reduced weight gains[73,74,96] or with decreased milk[42] and egg production[1,5,57,87]. In general, the palatability of the ration is thought to be the major consideration. Other studies have revealed no long-term effects of low level nitrate feeding trials in swine, sheep, cattle, and poultry.

The role of nitrate (nitrite) in abortions is controversial. Nitrate (nitrite) intoxication was suspected as the cause of bovine abortion[26,61] in various midwestern states in which cattle consumed forages containing approximately 1-percent potassium nitrate.

Some experimental studies with cattle have suggested that nitrate (nitrite) is of little significance[19,93] in the production of abortions in cattle, sheep, and swine. In contrast to these studies, an investigation of the lowland abortion syndrome[75,76,77] in Wisconsin suggested that nitrate (nitrite) does play a role in cattle abortion. Also, ruminants fed balanced rations[93,100] do not respond to the ingestion of nitrate (nitrite) as do cattle on a marginal or inadequate diet. The discrepancy of the lowland abortion experimental data and other experiments is attributed to the fact that the experimental animals used in the lowland abortion study were native cattle on an inadequate diet; hence, their response differed from cattle on a balanced ration. Unpublished data[100] revealed that when cattle on a balanced ration were fed levels of nitrate similar to those given to the cattle in lowland study, they did not abort and did not manifest placental lesions.

A number of investigators have shown that the long-term ingestion of sublethal nitrate (nitrite) results in a compensatory polycythemia[1,17,93] as a sequel to abnormal levels of methemoglobin.

UREA

Blood studies in experimental urea intoxication[22,23] reveal high ammonia levels with clinical signs of respiratory difficulty, excessive salivation, and frothing--presumably the results of severe alkalosis.

AMMONIA

Ammonia constitutes a potential hazard, primarily in the confinement rearing of swine. Whether NH_3 is of importance is currently under investigation at the Illinois Experiment Station. Preliminary work with experimental swine housed for four weeks in stainless steel units and subjected to an atmosphere containing 50 ppm of NH_3 resulted in mild conjunctivitis and blepharitis[100]. In addition, gross pathologic examination revealed mild inflammation of the turbinates and trachea. The lungs appeared to be normal. Histopathologic examination revealed a mild focal, chronic rhinitis, mild focal chronic tracheitis, and normal lungs.

OXIDES OF NITROGEN

Unconfirmed clinical reports[100] have attributed deaths of cats and dogs to "yellow gases," apparently derived from recently ensiled corn. The gases are believed to represent various oxides of nitrogen. Since necropsy data are not available, the significance of the reports is unknown. The toxicity of these compounds in animals may be similar to that of the "silo fillers"[71,88,98] disease in man.

HYDROXYLAMINE

Hydroxylamine may represent an intermediate metabolite in the breakdown of nitrite into ammonia. The importance[41,93] and potential hazard of this compound has been shown primarily in sheep in which a hemolytic anemia has been produced experimentally. The natural occurrence of this type of intoxication is unknown.

NITROSAMINES

Nitrosamines[55,95] are compounds formed by a reaction between nitrites and various classes of amines. This reaction can occur in a variety of foods and biological conditions.

Various N-nitrosamines and N-nitrosoamides have been shown in experimental laboratory animals to be carcinogenic[24,55,56,95]. They may also be mutagenic and teratogenic. Severe hepatic disease in Norwegian cattle[49] revealed dimethylnitrosamine (DMN) to be the probable cause. Indirect evidence suggested that batches of herring meal fed to cattle, sheep[70], and chicks resulted in severe hepatic disease and presumably was the result of a compound formed between nitrite and another component of the meal. Subsequent studies in sheep with DMN showed similar hepatic alterations. Hepatic disease has also been observed in mink and foxes[50] that were fed toxic herring meal which contained DMN.

MANNER OF DIAGNOSIS OR DETECTION

ACUTE NITRATE (NITRITE) INTOXICATION

A presumptive diagnosis is based on a history of excessive ingestion of the compound(s) with concomitant signs of hypoxia, brownish discoloration of the blood and membranes, and the occurrence of rapid death. Confirmation is usually based on increased methemoglobin[3,65], nitrate, and nitrite blood[29,51,90] levels. In addition, the suspect feed and water[64] is analyzed for nitrate (nitrite).

CHRONIC NITRATE (NITRITE) INTOXICATION

A clinical assessment of chronic intoxication poses a diagnostic challenge and is made after other disease processes are excluded. Additional evidence can be acquired through analyses of blood, milk, urine, water, and feed[37]. Methemoglobin values can also be used. However, differences resulting from delay in the analysis of blood samples[35] and from individual variation may limit such usage.

Other indirect analyses[36,72,86,96] that may suggest sublethal or chronic nitrate (nitrite) intoxication include the carotene and/or vitamin A level of serum and, if possible, of the liver; hemoglobin concentration; and the number of erythrocytes, essentially an assessment of polycythemia, reported as a result of the intoxication.

UREA

Presumptive diagnoses of urea poisoning are based on history[84], clinical and gross necropsy findings[97], and blood analyses characterized by elevated NH_3 levels and alkalosis.

AMMONIA

Although levels of 50 ppm are irritating to the mucous membranes of man, limited studies suggest that swine are otherwise essentially unaffected. The number of diagnoses, if any, of ammonia intoxication in animals is currently unknown.

OXIDES OF NITROGEN

In a few clinical reports, a presumptive diagnosis was based on a history of recent silo filling and the subsequent occurrence of a yellow-colored gas coming from the silo chute. It is believed that affected animals would probably suffer from extensive respiratory difficulty as a result of pulmonary edema--similar to that of man in "silo fillers" disease.

HYDROXYLAMINE

This intermediate compound of nitrate metabolism probably is of minimal importance as an intoxicant in ruminants, primarily in sheep. Analyses of rumen contents for this compound, if elevated above control animals under identical conditions, with a concomitant hemolytic anemia could conceivably have diagnostic significance.

NITROSAMINES

The presence of nitrosamines in various feeds can be confirmed by mass spectrometry[83] and chromatography[83]. The fact that nitrosamines are present in many human foods would suggest by analogy a comparable situation in animal feeds.

IMPORTANCE OF DAMAGE, AND INDICATIONS OF TRENDS

Acute nitrate (nitrite) intoxication in herbivora is relatively uncommon under modern methods of animal husbandry.

An outbreak of nitrate (nitrite) intoxication of cattle in Kansas[58] and Missouri[14] was associated with drought-affected corn. The utilization of nitrogenous fertilizers and herbicides in the Corn Belt, and the possibility of drought, present a potential hazard[94] for cattle if they consume affected corn stalks[58]. Since relatively few ears of corn would be produced under extreme drought, the role of either ear or shelled corn in chronic nitrate (nitrite) intoxication would probably be negligible.

Currently, considerable controversy exists regarding a possible increase in nitrate (nitrite) in the runoff[48] from fertilized fields and the creation of a potential environmental problem. Urea and hydroxylamine are thought to be of little importance.

The potential role of ammonia, either alone or in association with other gases emanating from "pits," remains obscure. Empirically, in confinement swine operations, reproductive problems, marginal weight gains, and respiratory disease have been attributed to the various gases, although experimental confirmation is lacking.

Perhaps one of the greatest potential hazards is that of the nitrosamines from the standpoint of carcinogenesis, mutation, and teratoma formation. Livestock as well as animal products used for human and pet food would be involved.

POSSIBLE SOURCES OF NITROGENOUS COMPOUNDS

The major source of nitrogenous compounds for herbivora is plants such as hays and grains. The role of contaminated water remains an enigma. For swine, NH_3 derived from wastes constitutes a potential hazard, the significance of which remains to be proven. Since nitrosation[95] may occur under a variety of conditions, the availability of feeds containing nitrite and various amines poses a potential hazard.

SUGGESTIONS

Current experimental and clinical evidence suggests that nitrate (nitrite) intoxication in herbivora is of limited occurrence, occurring primarily during periods of drought. The increased use of readily available nitrogenous fertilizers increases the hazard in the event of drought.

The role of nitrate (nitrite) in carotene, vitamin A metabolism, needs to be delineated more clearly, particularly in relation to cattle, sheep, and swine. The monitoring of nitrate (nitrite) levels in water should be expanded, and an assessment of concomitant disease problems in livestock should be made.

Since the current methodology for nitrosamine detection is laborious and expensive, better analytic procedures need to be developed. If possible, the relationship between nitrosamine levels and the induction of neoplasia should be established. The role and amounts of these compounds as mutagens and in teratoma formation and in connection with other disease problems also needs to be investigated.

REFERENCES

1. Adams, A.W., Emerick, R.J., and Carlson, C.W. 1966. Effects of nitrate and nitrite in the drinking water on chicks, poults, and laying hens. *Poultry Sci.* 45:1,215-1,222.

2. Asbury, A.C. and Rhode, E.A. 1964. Nitrite intoxication in cattle; the effects of lethal doses of nitrite on blood pressure. *Vet. Res.* 25:1,010-1,013.

3. Bajo, M., Mezencer, J., and Bartik, M. 1965. Certain quantitative relations of NO_3/NO_2 methemoglobin in farm animals. VI. The way blood samples are to be sent in for determination of methemoglobin content. *Folia Vet.* 9:65-71.

4. Bartik, M. 1964. Certain quantitative relations of NO_3 and NO_2 metabolism in farm animals with special regard to the origin and development of methemoglobinemia caused by NO_2 and the diagnosis of poisoning. I, II, III. *Folia Vet.* (Kosice) 8:83-93, 95-105, 111-122.

5. Bentley, A.B., Kinder, Q.B., Garner, G.B., and Savage, J.E. 1965. Effect of nitrate in water on performance of laying hens. *Poultry Sci.* 44:1,351.

6. Betke, K., Greinacher, I., and Hecker, F. 1956. Oxydation menschlicher und tierischer oxyhämoglobine durch natriumnitrit. *Arch. Exp. Pathol. Pharmacol.* 229:220.

7. Bloomfield, R.A., Hersey, J.R., Welsch, C.W., Garner, G.B., and Muhrer, M.E. 1962a. Gastric concentration of nitrate in rats. *J. Anim. Sci.* 21:1,019.

8. Bloomfield, R.A., Welsch, C.W., Garner, G.B., and Muhrer, M.E. 1961. Effect of dietary nitrate on thyroid function. *Science* (Washington) 134:1,690.

9. Bloomfield, R.A., Welsch, C.W., Garner, G.B., and Muhrer, M.E. 1962b. Thyroidal I^{131} metabolism in nitrate fed sheep. *J. Anim. Sci.* 21:988.

10. Bloomfield, R.A., Welsch, C.W., Garner, G.B., and Muhrer, M.E. 1962c. Thyroid compensation under the influence of dietary nitrate. *Proc. Soc. Exp. Biol.* 111:288-290.

11. Bloomfield, R.A., Welsch, C.W., and Muhrer, M.E. 1964. Overcoming nitrate induced thyroid inhibition with iodine. *J. Anim. Sci.* 23:1,207.

12. Bradley, W.B., Eppson, H.F., Beath, O.A. 1939. Nitrate as the cause of oat-hay poisoning. *J. Amer. Vet. Med. Assoc.* 94:541-542.

13. Bradley, W.B., Eppson, H.F., and Beath, O.A. 1940. Livestock poisoning by oat hay and other plants containing nitrate. Wyo. Agr. Exp. Sta. Bull. 241.

14. Case, A.C. 1957. Some aspects of nitrate intoxication in livestock. *J. Amer. Vet. Med. Assoc.* 130:323-329.

15. Cline, T.R., Hatfield, E.E., and Garrigus, U.S. 1962. Effects of potassium nitrate, alpha-tocopherol, thyroid treatments and vitamin A on weight gain and liver storage of vitamin A in lambs. *J. Anin. Sci.* 21:991.

16. Cline, T.R., Hatfield, E.E., and Garrigus, U.S. 1963. Effects of potassium nitrate, alpha-tocopherol, thyroid treatments and vitamin A on weight gain and liver storage of vitamin A in fattening lambs. *J. Anim. Sci.* 22:911-913.

17. Curtin, T.M. and London, W.T. 1966. Nitrate-nitrite intoxication in swine. *Proc. U.S. Livestock Sanit. Assoc.* 70:339-348.

18. Davidson, W.B., Doughty, J.L., and Bolton, J.L. 1941. Nitrate poisoning of livestock. *Can. J. Comp. Med. Vet. Sci.* 5:303-313.

19. Davison, K.L., Hansel, Wm., Krook, L., McEntee, K., and Wright, M.J. 1964a. Nitrate toxicity in dairy heifers. I. Effects on reproduction, growth, lactation and vitamin A nutrition. *J. Dairy Sci.* 47: 1,065-1,073.

20. Davison, K.L., McEntee, K., Wright, M.J., and Hansel, Wm. 1964b. Performance of pregnant ewes fed high nitrate forages. *J. Anin. Sci.* 23:903.

21. Davison, K.L. and Seo, J. 1963b. Influence of nitrate upon carotene destruction during *in vitro* fermentation with rumen liquor. *J. Dairy Sci.* 46:862-864.

22. Dinning, James S., Briggs, H.M., Gallup, W.D., Orr, H.W., and Butler, R. 1948. The effect of orally administered urea on the ammonia and urea concentration in the blood of cattle and sheep, with observations on blood ammonia levels associated with symptoms of alkalosis. *Am. J. Physiol.* 153:41-46.

23. Dinning, J.S., Briggs, H.M., Gallup, W.D., Ross, O.B., Moe, L.H., and Butler, R.L. 1949. Urea in livestock feeding. *J. Amer. Vet. Med. Assoc.* 114:90-92.

24. Druckrey, H., Preussmann, R., Ivankovic, S., and Schmahl, D. 1967. Organotropic carcinogenic effects of 65 different N-nitroso-compounds on BD rats. *Z. Krebsforsch.* 69:103-201.

25. Emerick, R.J., Embry, L.B., and Olson, O.E. 1963. Nitrate--Its effect on carotene and vitamin A. *Feed Age* (April):52-57.

26. Garner, G.B. 1958a. Learn to live with nitrate. Missouri Agr. Exp. Sta. Bull. 708.

27. Garner, G.B., O'Dell, B.L., Radar, P., and Muhrer, M.E. 1958b. Further studies on the effects of nitrate upon reproduction and vitamin A storage with rats and swine. *J. Anim. Sci.* 17:1213.

28. Greene, I. and Hiatt, E.P. 1954. Behavior of the nitrate ion in the dog. *Amer. J. Physiol.* 176:463-467.

29. Greweling, T., Davison, K.L., and Morris, C.J. 1964. Nitrate in body fluids: Determination of nitrate-N in bovine blood, urine and rumen liquor. *J. Agr. Food Chem.* 12:139-140.

30. Griffin, S.A., Henneman, H.A., and Reineke, E.P. 1962. The thyroid secretion rate of sheep as related to season, breed, sex, and semen quality. *Amer. J. Vet. Res.* 23:109-113.

31. Gwatkin, R. and Plummer, P.J.G. 1946. Toxicity of certain salts of sodium and potassium for swine. *Can. J. Comp. Med. Vet. Sci.* 10: 183-190.

32. Hale, W.H., Hubbert, F.J., and Taylor, R.E. 1961. The effect of concentrate level and nitrate addition on hepatic vitamin A stores and performance of fattening steers. *J. Anim. Sci.* 20:934.

33. Hanway, J.J., Herrick, J.B., Willrich, T.L., Bennett, P.C., and McCall, J.T. 1963. The nitrate problem. Iowa State Univ. Special Rpt. 34.

34. Hatfield, E.E., Smith, G.S., Neumann, A.L., Forbes, R.M., Garrigus, U.S., and Ross, O.B. 1961. Interactions of nitrite alpha-tocopherol and tapazole upon the vitamin A nutrition of lambs fed "high nitrate" silage. *J. Anim. Sci.* 20:676.

35. Helwig, D.M. and Setchell, B.P. 1960. Observations on the diagnosis of nitrite poisoning in sheep. *Aust. Vet. J.* 36:14.

36. Holst, W.O., Flynn, L.M., Garner, G.B., and Pfander, W.H. 1961. Dietary nitrite vs. sheep performance. *J. Anim. Sci.* 20:936.

37. Housholder, G.T., Dollahite, J.W., and Hulse, R. 1966. Diphenylamine for the diagnosis of nitrate intoxication. *J. Amer. Vet. Med. Assoc.* 148:662-665.

38. Heuper, W.C. and Landsberg, J.W. 1940. Experimental studies in cardiovascular pathology. I. Pathologic changes in the organs of rats produced by chronic nitrite poisoning. *Arch. Pathol.* 29:633-648.

39. Hutagalung, R.I., Chaney, C.H., Wood, R.D., and Waddill, D.G. 1968. Effects of nitrates and nitrites in feed on the utilization of carotene in swine. *J. Anim. Sci.* 27:83-87.

40. Jainudeen, M.R., Hansel, Wm., and Davison, K.L. 1965. Nitrate toxicity in dairy heifers. III. Endocrine responses to nitrate ingestion during pregnancy. *J. Dairy Sci.* 48:217-221.

41. Jamieson, N.D. 1958. Adverse effect of nitrate metabolic products on sheep growth. *Nature* 181:1,601.

42. Jones, I.R., Weswig, P.H., Bone, J.F., Peters, M.A., and Alpan, S.O. 1966. Effect of high-nitrate consumption and lactation and vitamin A nutrition of dairy cows. *J. Dairy Sci.* 49:491-499.

43. Jordan, H.A., Smith, G.S., Neumann, A. L., Zimmerman, J.E., and Brenman, G.W. 1963. Vitamin A nutrition of beef cattle fed corn silages. *J. Anim. Sci.* 22:738-745.

44. Keeney, D.R., Byrnes, B.H., and Genson, J.J. 1970. Determination of nitrate in water with the nitrate-selective ion electrode. *Analyst* 95:383-386.

45. Kilgore, L., Stasch, A.R., and Barrentine, B.F. 1964. Relation of ascorbic acid to nitrate content of turnip greens and to methemoglobin formation. *Amer. J. Clin. Nutr.* 14:52-55.

46. Koch, B.A., Parrish, D.B., and Sukhonthasarnpa, S. 1963. Effects of dietary NO_2 and NO_3 on growing swine. *J. Anim. Sci.* 22:840.

47. Kociba, R.J. and Sleight, S.D. 1970. Nitrate toxicosis in the ascorbic acid-deficient guinea pig. *Toxicol. Appl. Pharmacol.* 16:424-429.

48. Kohl, D.H., Shearer, G.B., and Commoner, B. 1971. Fertilizer nitrogen: Contribution to nitrate in surface water in a corn belt watershed. *Science* 174:1,331.

49. Koppany, N. 1964a. An outbreak of toxic liver injury in ruminants. Case reports, pathological-anatomical investigations and feeding experiments. *Nord. Vet. Med.* 16:305-322.

50. Koppang, N. 1966. A severe progressive liver disease in fur animals. I. Symptoms and organ changes. *Nord. Vet. Med.* 18:205-209.

51. Kühnert, M. 1967. Proposal for the determination of nitrate and nitrite compounds in biological material. *Mh. Veterinaermed.* 22:608-611.

52. Künzer, W., and Schultz, D. 1953. Zur aktivitat der reduzierenden fermentsysteme in den erythrozyten gunjger sauglinge. *Acta Haemat.* 9:346-358.

53. Lee, D.H.K. 1970. Nitrates, nitrites and methemoglobinemia. Nat. Inst. Environ. Health Sci., Research Triangle Park, N.C.

54. Lewis, D. 1951. The metabolism of nitrate and nitrite in sheep. *Biochem. J.* 49:149-153.

55. Lijinsky, W. and Epstein, S. S. 1970. Nitrosamines as environmental carcinogens. *Nature* 225:21-23.

56. Magee, P.N. and Barnes, J.M. 1967. Carcinogenic nitroso compounds. *Advan. Cancer Res.* 10:164-246.

57. Marrett, L.E. and Sunde, M.L. 1968. The use of turkey poults and chickens as test animals for nitrate and nitrite toxicity. *Poultry Sci.* 47:511-519.

58. Mayo, N.S. 1895. Cattle poisoning by KNO_3. Kan. Agr. Exp. Sta. Bull. 49.

59. Metcalf, W.K. 1960-61. A biochemical change in the blood in pregnancy and malignant disease. *Phys. Med. Biol.* 5:259-269.

60. Metcalf, W.K. 1961-62b. The sensitivity of intracorpuscular haemoglobin to oxidation by nitrite ions. II. Observations on pregnant women and in some pathological states. *Phys. Med. Biol.* 6:437-444.

61. Muhrer, M.E., Garner, G.B., Pfander, W.H., and O'Dell, B.L. 1956. The effect of nitrate on reproduction and lactation. *J. Anim. Sci.* 15:1,291.

62. Nason, A. 1962. Symposium on metabolism of inorganic compounds. II. Enzymatic pathways of nitrate, nitrite and hydroxylamine metabolisms. *Bacteriol. Rev.* 26:16-41.

63. Newsom, I.E., Stout, E.N., Thorp, F., Jr., Barber, C.W., and Groth, S.H. 1937. Oat hay poisoning. *J. Amer. Vet. Med. Assoc.* 90:66-75.

64. O'Donovan, P.B. and Conway, A. 1968. Performance and vitamin A status of sheep grazing high-nitrate pastures. *J. of Brit. Grassland Soc.* 23:228-233.

65. Oser, B.L. 1965. *Hawks' Physiological Chemistry*, 14th ed. The Blakiston Division, McGraw Hill Book Co., New York City.

66. Pfander, W.H., Garner, G.B., Ellis, W.C., and Muhrer, M.E. 1957. The etiology of nitrate poisoning in sheep. Missouri Agr. Exp. Sta. Bull. 637.

67. Rath, M.R. and Krantz, J.C., Jr. 1942b. Nitrites. IX. A further study of the mechanism of action of organic nitrates. *J. Pharmacol. Exp. Ther.* 76:33-38.

68. Rein, H., Ristau, O., Kupfer, E., and Jung, F. 1968. Nitrosohemoglobinemia in $NaNO_2$ poisoning. *Folia Haematol.* 90:176-181.

69. Ross, J.D. 1963. Deficient activity of DPNH-dependent methemoglobin diaphorase in cord blood erythrocytes. *Blood* 21:51-62.

70. Sakshaug, J., Sognen, E., Hansen, M.A., and Koppang, N. 1965. Dimethylnitrosamine; its hepatotoxic effect in sheep and its occurrence in toxic batches of herring meal. *Nature* 206:1,261-1,262.

71. Seaton, V.A. 1957. Pulmonary adenomatosis in cattle produced by nitrogen dioxide poisoning. *N. Amer. Vet.* 38:109-111.

72. Seerley, R.W., Emerick, R.J., Embry, L.B., and Olson, O.E. 1965. Effect of nitrate or nitrite administration continuously in drinking water for swine and sheep. *J. Anim. Sci.* 24:1,014-1,019.

73. Sell, J.L. and Roberts, W.K. 1963. Effects of dietary nitrite on the chick: growth, liver vitamin A stores and thyroid weight. *J. Nutr.* 79:171-178.

74. Sell, J.L., Roberts, W.K., and Waddell, D.G. 1963. Methemoglobinemia and reduced feed consumption due to feeding nitrite to chicks. *Poultry Sci.* 42:1,474-1,476.

75. Simon, J., Sund, J.M., Douglas, F.D., Wright, M.J., and Kowalczyk, T. 1959. The effect of nitrate or nitrite when placed in the rumen of pregnant dairy cattle. *J. Amer. Vet. Med. Assoc.* 135:311-314.

76. Simon, J., Sund, J.M., Wright, M.J., Winter, A., and Douglas, F.D. 1958. Pathological changes associated with the lowland abortion syndrome in Wisconsin. *J. Amer. Vet. Med. Assoc.* 132:164-169.

77. Simon, J., Sund, J.M., Wright, M.J., and Douglas, F.D. 1959. Prevention of noninfectious abortion in cattle by weed control and fertilization practices on lowland pastures. *J. Amer. Vet. Med. Assoc.* 135:315-317.

78. Smith, J.E. and Beutler, E. 1966. Methemoglobin formation and reduction in man and various animal species. *Am. J. Physiol.* 210: 347-350.

79. Smith, R.P. 1967. The nitrite methemoglobin complex--Its significance in methemoglobin analyses and its possible role in methemoglobinemia. *Biochem. Pharmacol.* 16:1,655-1,664.

80. Sokolowski, J.H., Garrigus, U.S., and Hatfield, E.E. 1961. Effects of inorganic sulfur on KNO_3 utilization by lambs. *J. Anim. Sci.* 20: 953.

81. Stoewsand, G.S. 1970. Influence of sex and dietary ascorbic acid on nitrate-induced methemoglobinemia in Japanese quail. *Proc. Soc. Exp. Biol. Med.* 133:1,166-1,168.

82. Sunderman, F.W., and Sunderman, F.W. 1964. *Hemoglobin, Its Precursors and Metabolites.* Lippincott, Philadelphia.

83. Telling, G.M., Bryce, T.A., and Althorpe, J. 1971. Use of vacuum distillation and gas chromatography, mass-spectrometry for determination of low levels of volatile nitrosamines in meat products. *J. Agr. Food Chem.* 19:93.

84. Tierney, M., and Genderen, D.V. 1967. Urea toxicity. *Iowa State Univ. Vet.* 29:147.

85. Tillman, A.D., Sheriha, G.M., and Sirny, R.J. 1965. Nitrate reduction studies with sheep. *J. Anim. Sci.* 24:1,140-1,146.

86. Tollett, J.T., Becker, D.E., Jensen, A.H., and Terrill, S.W. 1960. Effect of dietary nitrate on growth and reproductive performance of swine. *J. Anim. Sci.* 19:1,297.

87. Tomov, A. 1965. Effect of prolonged intake of NO_3 and NO_2 on hens and the quality of their eggs. *Vet. Med. Nauk.* 2:313-321.

88. U.S. Public Health Service. 1962. Toxicity of nitrogen dioxide. U.S.P.H.S. Pub. 956. Govt. Printing Office, Wash., D.C.

89. Wang, Li Chuan, Garcia-Rivera, J., and Burris, R.H. 1961. Metabolism of nitrate by cattle. *Biochem. J.* 81:237-242.

90. Watts, H., Webster, M., Chappel, A., and Leaver, D.D. 1969. Laboratory diagnosis of nitrate poisoning in sheep and cattle. *Aust. Vet. J.* 45:492.

91. Welsch, C., Bloomfield, R.A., Garner, G.B., and Muhrer, M.E. 1961. Effect of dietary nitrate on thyroid and adrenal gland weight. *J. Anim. Sci.* 20:981.

92. Welsch, C.W., Bloomfield, R.A., Garner, G.B., and Muhrer, M.E. 1962. Response of rats to low temperature and nitrate. *J. Anim. Sci.* 21: 1,032.

93. Winter, A.J., and Kokanson, J.F. 1964. Effects of long-term feeding of NO_3, NO_2 or hydroxylamine on pregnant dairy heifers. *Amer. J. Vet. Res.* 25:353-361.

94. Winton, E.F. 1970. Public health aspects of nitrate in drinking water. Presented at the American Water Works Assoc. 90th Annual Conf.

95. Wolff, I.A., and Wasserman, A.E. 1972. Nitrates, nitrites and nitrosamines. *Science* 177:15.

96. Wood, R.D., Chaney, C.H., Waddill, D.W., and Garrison, G.W. 1967. Effect of adding nitrate or nitrite to drinking water on the utilization of carotene by growing swine. *J. Anim. Sci.* 26:510-513.

97. Word, J.D., Martin, L.C., Williams, D.L., Williams, E.I., Panciera, R.J., Nelson, T.E., and Tillman, A.D. 1969. Urea toxicity in the bovine. *J. Anim. Sci.* 29: 786.

98. Wright, M.J. and Davison, K.L. 1964. Nitrate accumulation in crops and nitrate poisoning in animals. *In*: Advances in Agronomy. Academic Press Inc., New York City, 16:197-247.

99. Wyngaarden, J.B., Wright, B.M., and Ways, P. 1952. The effect of certain anions upon the accumulation and retention of iodine by the thyroid gland. *Endocrinology* 50:537-549.

100. Personal communication.

Human Health

Environmental and Health Effects of Nitrogenous Compounds

CARO E. LUHRS

METHEMOGLOBINEMIA

NITRATES, NITRITES ARE FOUND in drugs, food, and water. Man is continually exposed to small amounts of them. Usually, they cause no harm. In high concentrations and under special circumstances, however, they may cause illness and even death. Nitrates are generally toxic only by virtue of their potential for chemical conversion into nitrites.

ACUTE TOXICITY

The major clinical manifestation of acute nitrite toxicity is cyanosis (a bluish-purple discoloration of the skin and lips, which generally occurs within 1 to 2 hours after exposure and if unrelieved by oxygen therapy). There may be nausea, vomiting, and profuse sweating--in severe cases, lethargy--progressing to unconsciousness. Blood drawn from a patient with nitrite-induced cyanosis is a chocolate-brown color. These manifestations are explained by the oxidation of hemoglobin, the oxygen-carrying red pigment of blood, into methemoglobin, which is a brown pigment incapable of carrying oxygen. Death from asphyxia may result when large amounts of methemoglobin are formed and oxygen transport is severely impeded.

Methemoglobin is normally present in blood, constituting about 1 percent of the total hemoglobin of a healthy adult[17] and up to some 4 percent of the total hemoglobin of a healthy newborn infant[39]. Levels above 6 percent have been observed in normal babies with respiratory illness or diarrhea[24]. Cyanosis results when roughly 15 percent of the hemoglobin in blood is converted into methemoglobin. When methemoglobin constitutes 70

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percent or more of the total hemoglobin, death may occur[17]. Chemicals other than nitrites can cause methemoglobinemia. These range from sulfa drugs and phenacetin to the aniline dyes used in furniture polish, laundry-marking inks, and crayons. The condition may also exist in the absence of chemicals, as an inherited genetic defect[11].

As indicated previously, nitrates are toxic to man because of their potential for reduction into nitrites. Such a conversion of nitrates into nitrites may occur outside the human body (in nitrate-containing food of water prior to ingestion) or inside the human body (by the action of intestinal bacteria on ingested nitrates).

The form of nitrate/nitrite conversion that occurs during digestion requires very special conditions, ones that are likely to be present only in infants. The foremost prerequisite is the presence of nitrate-reducing bacteria in the upper gastrointestinal tract. Such bacteria are not normally present so high up in the intestinal tract. However, this circumstance may occur occasionally in infants, particularly those with gastrointestinal infections and a gastric pH insufficiently acid to kill the bacteria[5].

Several other factors explain why most cases of clinical nitrate-induced methemoglobinemia occur in infants: (1) the hemoglobin of a very young infant (so-called fetal hemoglobin) is oxidized twice as rapidly by nitrite to form methemoglobin as the hemoglobin of children and adults; and (2) the red blood cells of infants are not able to reduce methemoglobin into hemoglobin as well as that of adults[11].

CHRONIC TOXICITY

In contrast to the relative wealth of acute toxicity data in humans, reliable data are lacking on the physiologic effects, if any, of chronic nitrate/nitrite toxicity or of mild, non-cyanotic methemoglobinemia.

Studies in animals indicate that nitrates and nitrites may, on occasion, cause vitamin A deficiency and that nitrate may have an antithyroid effect by increasing the requirement for iodine[28]. There are no data available to indicate whether such effects can occur in man.

Abnormal changes on electroencephalograms have been observed in rats given 100 to 2,000 ppm of sodium nitrite each day for two weeks[40]. This obviously raises the question of the effect, if any, of chronically elevated methemoglobin levels on the human brain. One Russian study[32] purports to show a decreased response to visual and auditory stimuli in school children with a mean methemoglobin level of 5.3 percent of total hemoglobin. The study was poorly controlled and the conclusions, therefore, must be regarded as potentially unreliable. Patients with hereditary methemoglobinemia and mental retardation have been reported. However, the association may be coincidental. Most patients with hereditary methemoglobinemia do not have mental or neurologic abnormalities[17].

SOURCES OF NITRATES AND NITRITES

Drugs. Nitrates (nitroglycerin) and nitrites (amyl nitrite) have been used for over a hundred years for the relief of pain of angina pectoris. Methemoglobinemia associated with therapeutic use of cardiac nitrites (amyl nitrite and sodium nitrite) is rare. It has occurred, however, from the accidental ingestion of such drugs as in the case of eleven men who mysteriously turned blue after eating oatmeal that had been seasoned with sodium nitrite instead of salt.[13].

Although amyl nitrite and sodium nitrite are still used in the treatment of cyanide poisoning and in some diagnostic cardiac procedures, angina pectoris is more commonly managed by using one of the organic nitrates, such as nitroglycerin. These compounds allegedly do not cause methemoglobinemia[12].

Methemoglobinemia has been a rare complication in the use of nitrate-containing drugs such as bismuth subnitrate (an anti-diarrheal agent), ammonium nitrate (a diuretic), and silver nitrate (a compound used topically in the treatment of burns)[25,46,48].

Vegetables. Nitrates and nitrites occur in the human food supply, both naturally and as additives. Nitrates are natural constituents of plants. Many fresh vegetables (spinach, kale, beets, radishes, eggplant, broccoli, lettuce, celery, turnips, carrots, parsley, squash, cabbage, and cauliflower) may contain nitrates in high concentrations (over 3,000 ppm of nitrate)[19]. There may be great variations in nitrate content between samples of the same vegetable grown in different geographical locations. This is thought to be a reflection of differences in species and also of the differences in growth conditions, such as water, temperature, sunlight, and the nitrate content of the soil. In contrast to nitrate, the nitrite content of fresh vegetables is low[28]. But nitrate may be converted into nitrate during storage[33] by the action of bacteria or of a nitrate-reducing enzyme. Such an enzyme (nitrate reductase) has been identified in spinach leaves[31].

Despite the high nitrate content of a number of vegetables and the possibility for converting nitrate into nitrite during storage, there have been surprisingly few case reports of vegetable-induced methemoglobinemia in humans (less than fifty); only two in the United States. All have involved infants under one year of age. All, save for a single case report implicating commercially packed strained beets[28], have been attributed to the ingestion of stored, fresh spinach or carrots.

In the cases attributable to spinach[44,42,15], fresh spinach had generally been pureed and then stored at room temperature or refrigerated for a day or more before feeding. Home-prepared carrot soup was involved in sixteen cases that occurred in France, where carrot soup is an apparently well-known remedy for infant diarrhea. The soup had generally been stored for a day or more after preparation without refrigeration. In all cases, the municipal water used in making the soup was free of excessive concentrations of nitrates. The nitrate/nitrite conversion was supposed to have occurred either as a result of bacterial contamination of the soup or by virtue of a pre-existing gastroenteritis, which caused nitrate-reducing bacteria to be present in the infants' upper intestinal tracts[20]. One case of methemoglobinemia in an infant and attributed to home-prepared carrot juice has been noted in the United States. One fact of interest is that the carrots in question were grown without the use of nitrogen-containing fertilizer[18].

It is important to note that there has been only one case of methemoglobinemia attributable to commercially prepared vegetables, that one to strained beets[28]. Industry marketing data[45] for the year ending in June, 1972, indicate that 400 thousand jars of canned spinach, 500 thousand jars of canned beets, and 1.7 million jars of canned carrots were sold in the United States. Studies of canned baby-food spinach have shown only traces of nitrites, even after the jars had been stored open under refrigeration for 35 days. By contrast, nitrite accumulation does occur with storage of unprocessed fresh spinach, even under refrigeration[34].

Meat. Nitrates (saltpeter) and salt have been used as additives in the curing of meat since ancient times. The use of nitrite is comparatively recent, about 50 years old. It can be traced to the scientific observation that the typical reddish-pink color of cured meat was not due to nitrate, rather to the reduction of nitrate into nitrite and the subsequent reaction between nitrite and meat pigment to form nitrosylmoglobin, the characteristic pigment.

At present in the U. S., mixtures of nitrate and/or nitrite and salt are used in the curing of certain meat and fish products for three distinct purposes: color-fixation, flavoring, and protection against bacterial growth; particularly *Clostridium botulinum*. In some European countries, nitrates and/or nitrites are permitted as additives to cheese and flour as well as to fish and meat.

Cured meat and fish products play a prominent role in the American diet. They are popular because of their unique taste. Bacon without nitrates and/or nitrites would not taste like bacon. Cured pork and beef meat products (ham, bacon, salami, pastrami, corned beef, frankfurters, and the like) represent about a third of the total meat produced in the United States[7]. Cured fish products (chub, sable, and salmon) represent less than 2 percent of the dollar value of all processed fish products[26].

The maximum levels of these compounds permitted in the finished product are:

	Cured meat	Cured fish
	ppm	
$NaNO_3$	1,700	500
$NaNO_2$	200	200

Cases of methemoglobinemia have been reported in children and in adults as the result of an accidental use of excessive nitrate/nitrite in meat[30,2] and fish products[43]. There have been no case reports involving usage at permitted levels.

Water. The most common cause of methemoglobinemia is the consumption of water containing high levels of nitrates. This has accounted for many more cases than all other causes combined (nearly 2,000 reported in the U.S. and Europe). Methemoglobinemia of such etiology has been reported only in infants. There is one report in the literature of methemoglobinemia resulting from the use of nitrate-contaminated well water for peritoneal dialysis in an adult with kidney disease[3].

In addition to the factors outlined previously that make infants more susceptible than adults to nitrate-induced methemoglobinemia, an infant's total fluid intake per unit of body weight is much greater than an adult's. Thus, an infant consumes proportionately more nitrate than an adult. Moreover, boiling water for 10 to 15 minutes, which may occur during preparation of infant formula, tends to concentrate any nitrate present in the water.

The critical association between high concentrations of nitrates in the water used to prepare formula and methemoglobinemia in infants receiving formula was first made in 1945[4]. Since that time, approximately 2,000 such cases have been reported for North America and Europe. In the United States, only one case has been associated with water from a public water supply[52]; all the rest (about 300) have been due to well water.

Standards for nitrates in drinking water were set by the U.S. Public Health Service in 1962[51], limiting nitrate to 10 ppm expressed as nitrate/nitrogen (45 ppm expressed as nitrate). The 10 ppm nitrate/nitrogen level was set because there had been no reports in this country of infantile methemoglobinemia associated with the ingestion of water containing nitrate at levels below 10 ppm, and because it was a standard that could be met easily by most municipal water supplies.

After the publication of these standards, however, several reviews of the literature reported from other countries revealed that a small percentage of cases had occurred where the water nitrate/nitrogen content had been below 10 ppm[41,38]. It is important to note, however, that all these studies were retrospective--the water was sampled sometime after the infant became ill. Therefore, there is no certainty about the exact nitrate/nitrogen concentration in the water at the time of illness.

The adequacy of the 1962 standard is now being evaluated in several prospective studies designed to determine more specifically the nitrate levels in water required to cause elevated levels of methemoglobin and clinical evidence of methemoglobinemia in infants[53,14,39,54]. The preliminary results of these studies indicate that the 1962 standards provide adequate protection against clinical methemoglobinemia. However, subclinical elevations of methemoglobin have been found in infants with diarrhea or respiratory disease, consuming water with a nitrate content below this standard[39].

In addition to retrospective and prospective studies, hypothetical calculations have been made in order to predict potentially toxic levels of nitrate[54]. Such calculations are based on so many assumptions that they are of little value. The molar ratio of the nitrate-hemoglobin reaction, the efficiency of bacterial reduction of nitrate to nitrite and the rate of reduction of methemoglobin once it is formed are all unknowns that must be estimated in these hypothetical calculations.

NITROSAMINES

Nitrosamines are formed by the reaction between nitrites and organic compounds containing two, three, or four atoms of nitrogen (the so-called "secondary," "tertiary," and "quartenary" amines)[10]. Nitrites and/or precursor nitrates are present in foods, water, drugs[21] and human saliva[47]. Amines are found in foods, tobacco smoke, beer, tea, wine, toothpaste, and hundreds of drugs[21]. Certain nitrosamines have been found to be carcinogenic in animals. Some of these carcinogenic nitrosamines have been detected in food and tobacco. Concerns about potential hazards for human health arise from the possibility for (a) contact with preformed carcinogenic nitrosamines and (b) the formation of carcinogenic nitrosamines within the human body after exposure to precursor nitrites and amines.

TOXICITY

Nitrosamines have potent biological effects, including acute cellular injury (primarily involving the liver), carcinogenesis, mutagenesis, and teratogenesis. Approximately a hundred nitrosamines have been tested so far in animals. The vast majority are carcinogenic. Many species of animals and many different organs (the liver, esophagus, and kidneys) are susceptible to the cancer-producing effects of these compounds[23,29]. These effects can be elicited experimentally by various routes of nitrosamine administration (oral, intravenous, inhalation) by extremely low doses (ppm) of nitrosamines and, in some instances, after only one exposure[22].

Studies showing certain nitrosamines to be potent carcinogens in a wide range of animal species, including the monkey, suggest that the same compounds would also be carcinogenic for man. However, at present, there are no definitive data confirming this hypothesis.

Two epidemiological studies in Africa have attempted to link a geographically high incidence of cancer of the esophagus in humans with the ingestion of the juice of fruit from a solanaceous bush[8] and alcoholic spirits derived from fermented maize husks[27]--both purported to contain dimethylnitrosamine, a known carcinogen in animals. However, significant changes in laboratory methodology for confirming the presence of dimethylnitrosamine have occurred since these reports were published. Thus, the data are open to some question.

SOURCES OF NITROSAMINES

Food. Two nitrosamines, both known carcinogens in animals, have been detected in minute (ppb) quantities in some foods: dimethylnitrosamine in raw fish, smoked fish, nitrate/nitrite-treated smoked fish, cheese, and some nitrate/nitrite-treated meat products; and nitrosopyrrolidine in cooked bacon[6,49]. Except for cooked bacon, where nitrosopyrrolidine has been consistently found, nitrosamines are not always present in any given food product. Although nitrosamines are more likely to occur in nitrate/nitrite-treated food products, they may also occur in foods to which no nitrate/nitrite has been added.

Tobacco smoke. Several carcinogenic nitrosamines, including dimethylnitrosamine and nitrosopyrrolidine, have been identified in tobacco smoke[35,50]. There are some data to suggest that smoke from tobacco grown in soil treated with high levels of nitrogen is more likely to contain nitrosamines and to contain them in higher concentrations than smoke from tobacco grown in fields with a low nitrogen content[50].

Industrial exposure. Nitrosamines are formed in certain industrial processes. Important among these is the rocket-propellant industry, in which dimethylnitrosamine is an intermediate compound in the formation of dimethylhydrazine[24]. Acute human toxicity to dimethylnitrosamine through its use as a solvent has been reported[16]. Human exposure to mutagenic, teratogenic, and/or carcinogenic nitrosamines occurs in the manufacture of these compounds for research purposes, as well as in their subsequent use by research workers.

POTENTIAL FOR FORMATION FROM PRECURSORS

Of critical concern is the possible formation of carcinogenic nitrosamines in the human gut through the combination of ingested nitrites and amines. Such reactions have been demonstrated to occur both *in vitro*[9] and *in vivo* (in animals)[37]. Studies in humans fed nitrate and a noncarcinogenic nitrosamine precursor amine (diphenylamine) have shown that diphenylnitrosamine can be formed in the human stomach[36]. Nitrosamine determinations in these studies were made by thin-layer chromotography, a method now known to give false positive results. Unfortunately, there has been no confirmation of these data using the newer techniques of gas-liquid chromatography and mass spectrophotometry. However, this study raises the possibility that such precursor reactions may occur in man, leading to the formation of carcinogenic nitrosamines.

REDUCING HUMAN EXPOSURE TO NITROSAMINES AND TO NITROSAMINE PRECURSORS

As indicated in the part of this report dealing with nitrites and nitrates, one rationale for the use of these compounds in cured meat products is to prevent the growth of *Clostridium botulinum* organisms, thus protecting the consumer against botulism.

A joint research effort by the USDA, the FDA, and the American Meat Institute Foundation is in progress to determine the minimum levels of nitrate/nitrite necessary to be added to cured meat products in order to protect against botulism. If the quantities of nitrates and/or nitrites added to such good products could be significantly reduced, this might reduce the chances of nitrosamine formation.

Preliminary data from these studies indicate that, in the case of two cured meat products (canned ham and bacon), added nitrite, at levels only slightly below the 200 ppm currently permitted, is absolutely essential in preventing the formation of botulinus toxin. Nitrate, on the other hand, appears to have no effect in preventing such toxin formation[1].

SUGGESTIONS

1. Further prospective studies with infants are needed in order to determine more precisely the relationship between total daily nitrate/nitrite intake and levels of methemoglobinemia.

2. Long-term studies are needed to measure the effects, if any, of subclinical methemoglobinemia in humans.

3. The 1962 drinking water standards limiting nitrate to 45 ppm (10 mg/l of nitrate nitrogen) should not be relaxed.

4. The use of nitrate and nitrite in cured meat and fish products should be limited to those uses that are essential in inhibiting the growth of *Clostridium botulinum* and in obtaining the essential characteristics of cured meats. The Food and Drug Administration has proposed the banning of nitrate from most smoked, cured fish products. The U.S. Department of Agriculture is considering a lowering of the maximum level of nitrate permitted in cured meat products to 500 ppm and eliminating its use in those products where it is not essential.

5. Distilled or bottled water with a low nitrate content should be used for infant feeding in areas where the nitrate content in water is high.

6. The use of fresh vegetables with a potentially high nitrate content (especially spinach and carrots) should be avoided as much as possible in infant feeding--particularly when the vegetables have been stored prior to feeding or when the infants are less than six months of age or have diarrhea.

7. The nitrate content of water used for peritoneal dialysis in patients with kidney disease should not exceed 45 ppm (10 mg/l nitrate nitrogen).

8. The use of nitrate- and/or nitrite-containing drugs known to cause methemoglobinemia should be avoided where possible.

9. Further studies of the nitrosamine content of foods, beverages, and tobacco smoke should be undertaken.

10. Nitrate and nitrite in cured meat and fish products should be limited to only those uses and those quantities that are essential in inhibiting the growth of *Clostridium botulinum*.

REFERENCES

1. American Meat Institute Foundation/USDA/FDA communication. 1972. Washington, D.C.

2. Bakshi, S.P. *et al.* 1967. Sausage cyanosis--acquired methemoglobinemic nitrite poisoning. *NEJM,* 277:1,072.

3. Carlson, D.J. *et al.* 1970. Methemoglobinemia from well water nitrates: A complication of home dialysis. *Ann. Int. Med.*, 73:75.

4. Comly, H.H. 1945. Cyanosis in infants caused by nitrates in well water. *JAMA*, 129:112.

5. Cornblath, M. *et al.* 1948. Methemoglobinemia in young infants. *J. Pediat.*, 33:421.

6. Crosby, N.T. *et al.* 1972. Estimation of steam-volatile N-nitrosamines in foods at the 1 mcg/kg level. *Nature*, 238:343.

7. DeGraff, H. 1972. Personal communication. American Meat Institute, Washington, D.C.

8. DuPlessis, L.S. *et al.* 1969. Carcinogen in a Transkeian Bantu food additive. *Nature*, 222:1198.

9. Ender, F. *et al.* 1971. Conditions and chemical reaction mechanisms by which nitrosamines may be formed in biological products with reference to their possible occurrence in food products. *Zeit. Lebsmittel-Unter. Forsch.* 133.

10. Fiddler, W. *et a* . 1972. Formation of N-nitrosodimethylamine from naturally occurring quaternary ammonium compounds and tertiary amines. *Nature*, 236:307.

11. Finch, C.A. 1948. Methemoglobinemia and sulfhemoglobinemia. *NEJM*, 239:470.

12. Goodman, L.S. and Gilman, A.Z. 1965. *The pharmacological basis of therapeutics*, 4th ed. Macmillan Co. New York City.

13. Greenberg, M. *et al.* 1945. Outbreak of sodium nitrite poisoning. *Am. J. Pub. Health*, 35:1217.

14. Gunderson, D.H., *et al.* 1971. Preliminary Report, Washington County Nitrate Study--The effect of high dose nitrate on young children. EPA Office of Water Programs, Cincinnati, Ohio.

15. Holscher, P.M. *et al.* 1969. Methämoglobinämie bei jungen Sauglingen durch nitrithaltigen spinat. *Dtsch. Med. Wschr.*, 89:1,751.

16. Hunter, D. *The diseases of occupation*. Little Brown and Co. Boston, Mass., p. 593.

17. Jaffe, E.R. *et al.* 1964. Methemoglobinemia in man. *In*: Moore, C.V. and Grown, E.B. (ed.). *Progress in Hematology*, Vol. 4. Gruen and Stratton, New York City, p. 48-71.

18. Keating, J. 1972. Personal communication. St. Louis Children's Hospital, St. Louis, Mo.

19. Lee, D.K. 1970. Nitrates, nitrites, and methemoglobinemia. *Environ. Res.* 3:48.

20. L'Hirondel, J. *et al.* 1971. Une cause nouvelle de methemoglobinemia du nourrison: La soupe de carottes. *Ann. pediatr.* (Paris). 18:625.

21. Lijinski, W. 1971. Testimony before hearings, "Regulation of food additives and mecicated animal feeds," of the Subcommittee of Committee on Government Operations, House of Representatives. U.S. Govt. Printing Office, Wash., D.C.

22. Magee, P.N. *et al.* 1962. *J. Path. Bact.*, 84:19.

23. Magee, P.N. *et al.* 1967. *Adv. Cancer Res.*, 10:163.

24. Magee, P.N. 1972. Communication to an interdepartmental group on nitrates, nitrites, and nitrosamines.

25. Marcus, H. *et al.* 1949. Nitrate methemoglobinemia. *NEJM*, 240:599.

26. Martin, R. 1972. Personal communication. National Fisheries Institute, Washington, D.C.

27. McGlashan, M.D. *et al.* 1968. Nitrosamines in African alcoholic spirits and Oesophageal cancer. *Lancet*, 2:1,017.

28. National Academy of Sciences. 1972. *Accumulation of nitrate*, NAS-NRC, National Academy of Sciences, Washington, D.C., 106 p.

29. Nitrosamines: A jig-saw puzzle with missing pieces. 1968. *Food Cosmet. Toxic.*, 6:647.

30. Orgeron, J.D. *et al.* 1957. Methemoglobinemia from eating meat with high nitrite content. *Public Health Reports*, 72:189.

31. Paneque, A. *et al.* 1965. Flavin nucleotide nitrate reductase from spinach. *Biochim. Biophys. Acta.* 109:79.

32. Petukhov, N.I. *et al.* 1970. Investigation of certain psychophysiological reactions in children suffering from methemoglobinemia due to nitrates in water. *Hyg. Sanit.*, 35:29.

33. Phillips, W.E.J. 1968. Changes in the nitrate and nitrite contents of fresh and processed spinach during storage. *J. Agr. Food Chem.* 16:88.

34. Phillips, W.E.J. 1971. Naturally occurring nitrate and nitrite in foods in relation to infant methaemoglobinaemia. *Fd. Cosmet. Toxicol.* 9:219.

35. Rhoades, J.W. *et al.* 1972. N-dimethylnitrosamine in tobacco smoke condensate. *Nature* 236:307.

36. Sander, J. *et al.* 1969. Bacterial reduction of nitrate in the human stomach as a cause of nitrosamine formation. *Arzheimittelforschung*, 19: 1,031.

37. Sander, J. 1971. Studies on formation of cancerogenic nitroso compounds in the stomach of experimental animals and their significance for man. *Arzheimittelforschung*, 21:1,572.

38. Sattelmacher, P.G. 1962. Methämoglobinämie durch nitrate in trinkwasser. *Schriftenreiche des Vereins fur Wasser Bodenund Lufthygiene*, No. 21.

39. Shearer, L.A. *et al.* 1972. Methemoglobin levels in infants in an area with high nitrate water supply. Calif. State Dept. of Public Health (preprint).

40. Shuval, H.I. *et al.* 1972. Epidemiological and toxicological aspects of nitrates and nitrites in the environment. *Am. J. Pub. Health*, 62:1,045-1,072.

41. Simon, C. *et al.* 1964. Uber vorkommen, pathogenese und moglichkeiten zur prophylaxe der durch nitrit verusachten methämoglobinamie. *Zeitschrift fur Kinderheilkunde*, 91:124.

42. Simon, C. 1966. L'intoxication par les nitrites après ingestion d'épinards. *Arch. Francaises de pediatrie* 23:231.

43. Singley, T.L. 1962. Secondary methemoglobinemia due to the adulteration of fish with sodium nitrite. *Annals of Int. Med.*, 57:800.

44. Sinios, V.A. *et al.* 1965. Die spinatvergiftung des sauglings. *Dtsch. Med. Wschr.* 90:1,856.

45. Stewart, R.A. 1972. Personal communication. Gerber Products Co., Fremont, Michigan.

46. Strauch, B. *et al.* 1969. Successful treatment of methemoglobinemia secondary to silver nitrate therapy. *NEJM*, 281:257.

47. Tannenbaum, S.R. 1972. Massachusetts Institute of Technology. Communication to interdepartment group on nitrates, nitrites, and nitrosamines.

48. Ternberg, J.L. *et al.* 1968. Methemoglobinemia: A complication of silver nitrate treatment of burns. *Ped. Surgery*, 63:328.

49. USDA/FDA. 1972. Communication to an interdepartmental group on nitrates, nitrites, and nitrosamines.

50. USDA/HEW/British American Tobacco Laboratory, collaborative research. 1972. Personal communication.

51. U.S. Public Health Service. 1962. Drinking water standards. Public Service Pub. 956.

52. Vigil, J. *et al.* 1965. Nitrates in municipal water supplies cause methemoglobinemia in infants. Public Health Reports, 80:1,119.

53. Winton, E.F. *et al.* 1969. Preliminary report: Field study on nitrate in drinking water and infantile methemoglobinemia. U.S. Public Health Service, Cincinnati.

54. Winton, E.F. *et al.* 1971. Nitrate in drinking water. *J. Amer. Water Works Assn.* 63:95.

Analytical Procedures

MARY K. ELLIS

THE NITROGENOUS COMPOUNDS present in the environment and used as pollutant indicators are ammonia, nitrate, nitrite, nitrosamines, and other organic compounds (amino acids, polypeptides, and proteins). There are no universal standard methods for the determination of these compounds. The methods generally used for water and food are those given in Table 1. For air and soils, water extracts, except for ammonia in soils, are made from the sample and a selective method of water analysis is used.

The analysis of nitrogenous compounds, with exception of nitrosamines, depends on:

1. A color resulting from its reaction with another compound to form a color complex, or
2. Direct titration of the nitrogen compound employing the use of a color indicator for an acid-base, end-point reaction.

To identify trace amounts of nitrosamines requires sophisticated and very expensive instrumentation. The mass spectrometer is, at present, the ultimate tool in the identification of N-nitroso compounds[5]. The Food and Drug Administration, the Department of Agriculture, and the Department of the Interior have this capability but have limited their analyses to fish and meat products.

Of the three methods being used for the detection of ammonia, the Nessler reagent is the conventional one for low levels in the range of 0.05-2 mg $N\text{-}NH_3/l$. This depends on the formation of a complex of mercuric ammono-basic iodide, which is red-brown in color. The intensity of the color caused by ammonia varies from yellow to brown.

$$HgI_2 + NH_3 \rightarrow Hg(NH_2)I + 2KI + HI$$

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A more recent method involves the development of an intensely blue compound, indophenol. Referred to as the phenate or phenolate method, the procedure has been automated[4], and requires only two minutes per sample analysis. In this method, ammonia reacts with hypochlorite and phenol in the presence of a manganous salt catalyst. The sensitivity of this method is in the range of 0.01-20.0 mg $N-NH_3$ per liter.

The titration method is the choice for samples containing more than 1.0 mg $N-NH_3/1$ and can be used on samples containing less. The principle is the titration of the ammonia--collected in a boric-acid solution, with sulfuric acid, using a color indicator for determining the end-point.

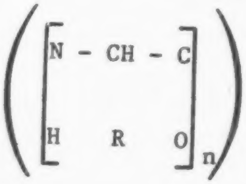
The Nessler method may be performed without prior distillation if the sample is free of interferences. Ca, Mg, Fe, certain organic compounds, sulfide, excess alkalinity, excess acidity, color, and turbidity are among the most common interferences for the detection of ammonia. Distillation will remove most of the interferences except sulfide, which must be precipitated prior to distillation. The distillate is collected in boric acid for the Nessler and titrimetric methods, and in sulfuric acid for the phenate method.

The two colorimetric methods require the use of a colorimeter to read the color intensities, and preparation of standards in the detectable range is necessary. In the automated phenolate procedure, a Technicon-autoanalyzer or its equivalent is also required.

As in the choice of methods for ammonia, the methods for nitrate determinations depend on the concentration of the nitrate in the sample and its matrix. Samples containing 5 mg of NO_3^- or less may be tested by direct nitration of brucine, phenoldisulfonic acid, or chromotropic acid. The choice of method for waste and saline waters is the alkaloid, brucine. This method is critically dependent on heat control at 100^{o}[4] for the development of the resulting complex. The interferences that can be eliminated include the color of the samples due to the high acidity of the reaction, salinity, oxidizing or reducing agents, residual chlorine, iron, and manganese. The phenoldisulfonic acid and chromotropic acid methods are grossly affected by turbidity, and are subject to

Table 1. GENERAL METHODS OF ANALYSIS FOR NITROGENOUS COMPOUNDS

- Nitrate-Ammonia (NH_4^+, NH_3)
  - Nesslerization[1,2,3,4]
  - Phenolate[1,4]
  - Titration[1,2,3,4]
- Nitrogen-Nitrate (NO_3^-)
  - a. Direct nitration
    - Brucine[1,3,4]
    - Phenoldisulfonic acid[1,2,4]
    - Chromotropic acid[1]
  - b. Nitrate reduction
    - Cd-reduction[1,2,4]
    - Hydrazine[4]
    - Devarda's alloy[3]
    - Xylenol-reduction[2]
    - Zn-reduction[1]
  - c. Direct method
    - Ultraviolet spectrophotometric[1]
- Nitrogen-Nitrite (NO_2^-)
  - Diazotization-coupling (Greiss reaction)[1,2,3,4]
  - KI reduction[2]
- Nitrogen-organic



$$\left(\left[\begin{array}{ccc} N - & CH - & C \\ H & R & O \end{array}\right]_n\right)$$

  - Kjeldahl[1,2,3,4]
- Nitrosamines-volatile (R_2-N-NO_2)[9]

Table 2. SUMMARY OF METHODS OF ANALYSIS USED BY ENVIRONMENTAL PROTECTION AGENCY

Nitrogen form	Method	Application	Interferences (c)	Sample size	Sensitivity (N/l)	Precision accuracy*
Ammonia	Distillation Nesslerization Titration (H_2SO_4)	A,B,C	Ketones, Aldehydes Alcohols Hydrazine Chloride ion Mercury, cyanide	500 ml	.05 to 1 mg 1.0 to 24 mg	p. 140
	Automated phenolate	A,C	Mercury Copper Magnesium pH	2.90 ml/min	.01 to 20 mg	p. 145
Organic total	Kjeldahl Nesslerization Titration	A,B,C	None	500 ml	11 mg 1 mg	p. 155 to 156
	Semiautomated (phenolate)	A,C	None	2.90 ml/min	1 to 10 mg	NA
	Automated (phenolate)	A,B,C	Iron, chromium Copper ions	For A = 2.50 ml/min For C = 1.60 ml/min	.05 to 2 mg	p. 162

(cont'd)

Table 2 (cont'd)

Nitrogen form	Method	Application	Interferences (c)	Sample size	Sensitivity (N/1)	Precision accuracy*
Nitrate	Brucine	A,B,C	Temperature Dissolved organics Salt Oxidation-reduction agents Chloride ion Iron Manganese	10 ml	0.1 to 2 mg	p. 174
Nitrate - nitrite	Automated (a) Cd-reduction (b) Sulfanilamide reagent (diazotization-coupling)	A,C	NH_3, primary amines Metal ions (hg, Cu)	1.60 ml/min	0.5 to 10 mg	p. 181 to 182
	Automated (a) Hydrazine reduction (b) Diazotization coupling	A,B	Tolerates high concentrations of interfering ions	2.90 ml/min	0.5 to 1 mg	p. 189 to 190
Nitrite	Diazotization-coupling	A,B,C	Concentration 1,000xNO_2 pH	50 ml	0.5 to 1 mg	NA

A--Surface water.

B--Domestic and industrial waste.

C--Saline waters.

(a) $NO_2 + NO_3$ a-b=NO_3

(b) NO_2

(c) Most of the interferences are eliminated.

* Reference to pages of the Manual.

NA Not available.

Reference: *Methods for Chemical Analysis of Water and Wastes*, 1971, Water Quality Control Laboratory, Water Quality Office, Environmental Protection Agency, Cincinnati, Ohio, p. 134-203.

Table 3. SUMMARY OF METHODS OF ANALYSIS USED BY THE DEPARTMENT OF INTERIOR

Nitrogen form	Method	Application	Interferences (c)	Sample size	Sensitivity (N/1)	Precision accuracy*
Ammonia	Distillation	Natural waters	Ca, Mg, Fe (a) Sulfide (c) Distilled organic compounds (e)	500 ml	<2 mg NH_3, NH_4^+/L	NA (i)
	Titration	Natural waters	Ca, Mg, Fe (a) Sulfide (c) Distilled organic compounds (e)	500 ml	>2 mg NH_3 NH_4^+/L	NA (i)
Nitrate	Brucine	Colorless waters	Organic color NO_2^- (b) Oxidizing and reducing agents Cl^- (f)	10 ml	<5 mg NO_3^-/L	.09-.11 mg/l (g)
	Reduction (Devarda's alloy)	Colorless waters	Organic color NO_2^- (b) Oxidizing and reducing agents Cl^- (f)	10 ml	>30 mg NO_3^-/L	.09-.11 mg/l (g)

(cont'd)

Table 3 (cont'd)

Nitrogen form	Method	Application	Interferences (c)	Sample size	Sensitivity (N/1)	Precision accuracy*
Nitrite	Diazotiazation	Natural waters	None	50 ml	<4 mg NO_2^-/L (d)	
Organic nitrogen	Kjeldahl	Natural waters	Ca, Mg, Fe (a)	500 ml	<2 mg N/L (d)	NA

(a) Eliminated by distillation.
(b) Eliminated by sulfanilic acid.
(c) Precipitated by lead carbonate.
(d) Higher cmc can be diluted.
(e) Distill sample into H_3BO_3 and titrate H_2SO_4.
(f) Eliminated by sodium arsenate.
(g) Standard deviation.
(h) Use residue of NH_3 nitrogen.
(i) Not available.

Reference: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," *Techniques of Water-Resources Investigations of the United States Geological Survey*, Book J, Chapter A1, 1970, p. 116-124.

Table 4. SUMMARY OF METHODS OF ANALYSIS USED BY THE FOOD AND DRUG ADMINISTRATION

Nitrogen form	Method	Application	Sample size	Sensitivity	Precision
Nitrate (a) Nitrite (a)	(A) Cd reduction → NO_2 (B) Sulfanilamide reagent $[A=NO_3+NO_2, B=NO_2, A-B=NO_3]$	Animal feeds	5 g	10-100 ppm nitrate N	NA
Nitrite (b)	Diazotization and coupling (Sulfanilic acid and Greiss reagent)	Flours	2 g	0.6 to 1.2 ppm nitrite N	NA
Nitrite (c)	Reduction with KI and titration with sodium thiosulfate	Dry curing mix or curing pickle	50 g	1% $NaNO_3$	NA
Nitrate (d)	Nitration of xylenol distillation and color development	Meat and meat products	5 to 10 g	5 to 500 ppm	± 50 ppm*
Nitrite (e)	Modified Greiss	Cured meats	5 g	NA	NA

*Provided by the staff of the USDA Meat and Poultry Laboratory.

NA, Not available.

(a) 7.033-7.039, JAOAC, 51, 763 (1968).
(b) 14.037-14.038, JAOC, 34, 273 (1951).
(c) 20.063-20.065, JAOAC, 47, 395 (1964).
(d) 24.011-24.013, JOAC, 18, 459 (1935); 22, 596 (1939).
(e) 24.014-24.015, JOAC, 8, 696 (1925); 35, 344 (1952).

Reference: These methods are contained in the Journal of AOAC, Vol. 48, No. 5, 1965. The original date of publication is given to emphasize that the analytical procedures are not new.

A summary of the methods of analysis used by the Environmental Protection Agency, the Department of the Interior, and the Food and Drug Administration for nitrogen analysis appears in Tables 2, 3, and 4, respectively, and includes the sensitivities. The precision and/or accuracy is either not available or has been determined by using a limited number of analyses.

The present methods of analyzing nitrogen for the ammonia, nitrate, nitrite, and organic nitrogen carry with them subjective error within every step of the procedure. These errors are compounded by the matrix of the sample, the temperature, and time, the preparation of standards, the purity of materials, a dilution factor, the addition of reagents, recovery, and human error. In addition, the organic nitrogen method eliminates the detection of amines, hydrazones, oximes, carbazones, and other organic nitrogen compounds. One of these groups, the amines, is a precursor to the formation of the nitrosamines.

The analysis for nitrosamines is restricted to those which are volatile. But the method is both sensitive and specific.

In consideration of the limitations of present analytical methods, and the paucity of basic data on the identity and concentration of organic nitrogen compounds in the environment, the following research projects are suggested for initiation or continuation:

1. Develop new methods of detection for nitrates and nitrites, and extend the method development for N-nitrosamines. These health hazards have now reached unacceptable levels in one or more phases of our environment.
2. Identify the concentrations of all organic nitrogen compounds in our water and in the atmosphere.
3. Establish the health hazards presented by the organic nitrogen compounds found in the water and the atmosphere; also, subsequent method development, for example, secondary amines as precursors of N-nitrosamines. (Consideration should be given to the clarification of the misnomers "organic-nitrogen" method and "total organic-nitrogen" method.)
4. Study nitrosamine formation in watersheds, particularly in areas near slaughter houses and meat-processing plants.

5. Study the basic amines present in foods, the amines that react with nitrites to form carcinogenic N-nitrosamines.

REFERENCES

1. *Standard Methods for Examination of Water and Waste Water*, 13th ed. 1970. American Public Health Assoc., American Water Works Assoc., Water Pollution Control Federation.
2. *Official Methods of Analysis*, Assoc. of Official Analytical Chemists, 11th ed., 1970.
3. *Methods of Collection and Analysis of Water Samples for Dissolved Minerals, Gases, Techniques of Water Resources Investigations of U.S. Geological Survey*, Book 5, Chap. A-1. 1970. p. 116-124.
4. *Methods for Chemical Analysis of Water Wastes, 1971.* Water Quality Control Laboratory, Water Quality Office. EPA, Cincinnati, p. 134-203.
5. *Report of Subcommittee on Analytical Methods for Nitrosamines.* International Agency for Research on Cancer.
6. *Review on the Chemistry and Toxicology of Nitrites, Nitrates and Nitroso Compounds (Nitrosamines).* Aug. 28, 1970. FDA (internal document).
7. Scanlon, R.A. and Libbey, L.M. N-Nitrosamines Not Identified from Heat Induced D-Glucose/L-Alanine Reactions. *J. Agri. Food Chem.*, Vol. 19, No. 3, 1971, p. 570-571.
8. Fazio, Thomas; Damico, Joseph N.; Howard, John W.; White, Richard H.; and Watts, James O. Gas Chromatographic Determination and Mass Spectrometric Confirmation of N-Nitrosodimethylamine in Smoke-Processed Marine Fish. *J. of Agri. Food Chemistry* 19(3): 250-53, March-April 1971.
9. Fazio, Thomas; Howard, John W.; and White, Richard. *Multideotion Method for Analysis of Volatile N-Nitrosamines in Foods.* In Nitroso-compounds, Analysis and Formation. Proceedings of a Conferency, World Health Organization, International Agency for Research on Cancer, Heidelberg, Germany. Oct. 13-15, 1971. p. 16-24.
10. Stanford, George, Agri. Res. Serv., Beltsville, Md. (private letter).
11. Kohl, Daniel H.; Shearer, Georgia; and Commoner, Barry. Contribution of Fertilizer to Nitrogen to Nitrate in Surface Water in a Cornbelt Watershed. *Science* 174, Dec. 1971.
12. Dzubay, Thomas. Div. of Chem. and Physics, Air Analytical Methods Branch, EPA, North Carolina (private communication).

13. Jaye, Dr. Frederic, Div. of Chem. and Physics, Source Emission Measurement Branch, EPA, Research Triangle, N.C. (Private communication.)

14. Hollander, Jack, Lawrence-Berkeley Labs., Berkeley, Calif. (Private communications).